RARE EARTH ELEMENTS IN AUSTRALIAN SEDIMENTS

by

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Statement

The analytical data and conclusions presented in this thesis are my own unless otherwise acknowledged in the text.

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Abstract

A suite of 53 Australian sedimentary rocks, ranging in age from Archaean to Cenozoic, were analyzed for the rare earth elements in order to detect any secular changes in rare earth distribution. The abundances of Th, U, Hf, Ba and Cs were also determined. The samples analyzed were mainly shales, greywackes and subgreywackes.

Most of the samples show rare earth distribution patterns similar to those previously reported for composites of North American and European Palaeozoic shales. These samples, which range in age from Middle Proterozoic to Cenozoic, show remarkably constant relative rare earth patterns and are hereafter referred to as the post-Archaean sediments. The post-Archaean sediments are characterised by almost constant negative Eu anomalies (average $Eu/Eu^* = 0.67 \pm 0.05$) relative to chondrites. The ratios of light to heavy rare earths are also approximately constant (average $\Sigma LREE/\Sigma HREE = 9.7 \pm 1.8$). In contrast to this, the Archaean sediments of the Kalgoorlie area, Western Australia and a suite of Devonian volcanic greywackes show large enrichments in Eu relative to the post-Archaean sediments and values of $\Sigma LREE/\Sigma HREE$ which are outside the range shown by the post-Archaean sediments.

The absolute abundances of the rare earths are generally higher in the younger sediments than in the older sediments. There is a suggestion that the absolute abundances of the rare earths in clastic sediments have gradually increased throughout time.

The almost constant nature of relative rare earth distribution patterns shown by the post-Archaean sediments is apparently due to the efficiency with which upper crustal material is mixed in the sedimentary cycle. Specific features of this "upper crustal" rare earth pattern suggest that the upper crust is a product of crustal stratification via partial melting processes in the crust. For example, a negative Eu anomaly in the overall upper crust is consistent with the preferential

retention of Eu in the lower crust by plagioclase, since plagioclase is usually a stable mineral phase during partial melting at crustal depths. Since no secular change in relative rare earth distribution was detected in the post-Archaean sediments, a uniform process of crustal growth and evolution seems to have operated over the past 1500 million years. The trend of increasing absolute abundnaces of the rare earths through time, if real, may possibly be related to a gradual reduction in the average degree of partial melting in processes of magma genesis.

The rare earth distribution patterns shown by the Archaean sediments are consistent with the derivation of these sediments from bimodal mixtures of detritus from the mafic and Na-rich felsic rocks in the Kalgoorlie area. The felsic rocks which served as source material for the sediments are characterized by large depletions in the heaviest rare earths and do not show negative Eu anomalies relative to chondrites. These features are interpreted as due to an origin of the felsic rocks by partial melting of tholeiitic basalts at depths greater than 40 km. The differences in rare earth distribution patterns between the Archaean and post-Archaean sediments suggest that the processes responsible for crustal development in the Archaean were not strictly analogous to those operating since the Middle Proterozoic.

A comparison of the average rare earth distribution pattern of the post-Archaean sediments with those shown by Australites supports the hypothesis that the parent materials of these tektites were clastic sediments or soils.

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Acknowledgements

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Chapter 1

Introduction

Thesis objective

This thesis reports the results of a study of rare earth element distributions in Australian sedimentary rocks. The primary object is to search for possible changes in rare earth distribution in the upper continental crust through time. Sediments represent the results of a crustal mixing process, and so are amenable to the study of compositional trends in the upper crust. Changes through time in major element chemistry of the important sedimentary rock types have been reported (Garrels and Mackenzie, 1971; Ronov, 1972). It is not certain if some of these changes are due to sedimentary recycling, or to more fundamental changes in the composition of the crust. The rare earth distribution of sediments is assumed to represent that of the upper continental crust (Haskin et al., 1966). Thus, by analyzing sediments of different ages it may be possible to detect changes in the rare earth distribution of the upper crust. These changes might correspond to changes in the relative amounts of the different types of igneous rocks contributing to the crustal composition. Most common igneous rock types have distinct rare earth distribution patterns, and the well known chemical coherence of the rare earths makes them more resistant than other elements to fractionation by weathering. Thus, the rare earths are sensitive to lithological change, and their distribution in the upper crust can be measured in sediments. This makes them unique among the elements, and suited for this type of study.

Similar studies have been made on sediments from other continents (Wildeman and Haskin, 1973; Wildeman and Condie, 1973).

The approach was to analyze a suite of young sediments and of ancient sediments, in order to search for differences between the two extremes. No rare earth data on Australian sediments has appeared, although this continent has an abundance of ancient sediments. In this study I have included samples from nearly every major period in geologic time, in order to obtain a more detailed view of possible trends. The sediments range in age from about 2800 to 50 million years. In most previous investigations the object of sample selection has been to include as many different types of sedimentary rocks as possible (shales, various types of sandstones, carbonates and ores). Many of the samples were composites of rocks from different formations. In this study I have attempted to use only clastic sediments. The use of composite samples has been avoided. Major element chemistry and bulk mineralogy were available for each sample used in the study.

Another important object of this thesis is to evaluate the usefulness of sedimentary rare earth data in solving other geological problems. The possibility of using the rare earths as indicators of sedimentary provenance is considered. The effect of weathering during deposition on rare earth distribution is also investigated.

The average sedimentary rare earth pattern deserves separate attention. If, as we assume, the sedimentary rare earth patterns are representative of the upper crust, then they may have implications for theories on the genesis of the upper and lower crust. This possibility is explored in the light of recent theories of magma genesis.

Rare earth chemistry

The term "rare earth", as used here, refers to the lanthanide series of elements (La-Lu), ranging in atomic number from 57 to 71. The element yttrium (atomic number 39) is included in the rare earth

group, because its geochemical behaviour is quite similar. The chemical similarity of the lanthanides is due to the valence electron configuration remaining unchanged while the 4f electron energy level is being filled. The net effect of adding another proton to the nucleus and the shielding effect of another 4f electron, is a significant reduction in ionic radius with increasing atomic number. The ionic radii of the lanthanides thus decreases from 1.06 $\overset{o}{A}$ for La^{3+} to 0.85 $\overset{o}{A}$ for Lu^{3+} (Templeton and Dauben, 1954). The ionic radius for Y^{3+} is 0.88 $\overset{o}{A}$ (Zachariasen, 1954), which should make it close to Er and Ho (0.88 $\overset{o}{A}$ and 0.89 $\overset{o}{A}$) in geochemical behaviour. Fig.1.1 shows a plot of lanthanide atomic numbers versus ionic radii, and this clearly shows the nearly linear relationship which is the basis of rare earth geochemical behaviour. The only common exceptions to a stable +3 oxidation state for the rare earths in geological samples are Eu and Ce. Eu may be reduced to the +2 oxidation state, which causes its geochemical behaviour to resemble that of Sr^{2+}, since the ionic radius of both is about the same. The only common rock forming minerals known to selectively retain Eu in preference to the other rare earths are the feldspars (Schnetzler and Philpotts, 1970). Ce can be oxidized to the +4 oxidation state, but examples of this in rocks are rare.

The "light rare earths" (La-Sm) belong to that group of elements, which due to their large ionic radii and/or high charge, are strongly excluded from most major minerals during partial melting or fractional crystallization processes. They are partitioned into the melt, which results in them being concentrated in the last phases to crystallize. They are commonly found in geochemical association with elements such as Th, U, Rb, K and Zr. The smaller ionic radii of the "heavy rare earths" (Gd-Lu) enables them to occupy lattice sites in some major minerals (Cullers et al., 1973). It is assumed that Ca^{2+}

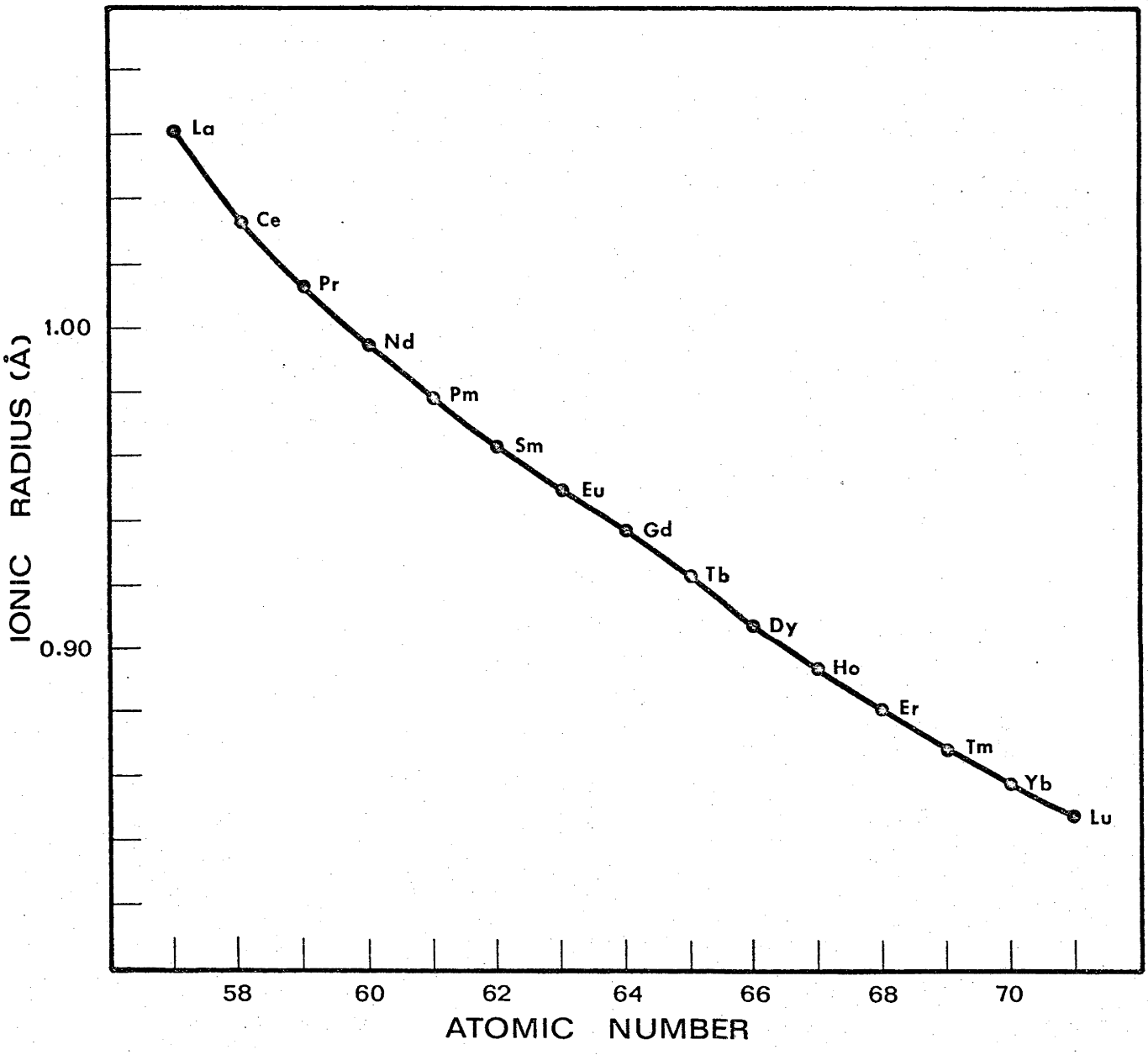

Fig. 1.1 The relationship of ionic radius to atomic number for the rare earth elements. Ionic radii are from Templeton and Dauben (1954).

is the only major element cation for which the heavy rare earths can substitute (Taylor, 1964). As a result, the heavy rare earths usually behave as a more coherent group, and are less enriched in the upper crust than the light rare earths. Eu, when not enriched or depleted due to its ability to enter the 2+ oxidation state, is transitional between the two groups.

Historical background

Prior to 1960 most geochemists considered that the rare earth elements were not subject to serious fractionation in the earth. Thus it should still preserve its initial distribution pattern (for a discussion of early views see Taylor, 1960). Early studies of the rare earths, by Minami (1935) in sediments and by Noddack (1935) in chondrites, indicated that a large difference existed in rare earth distribution between the earths crust and chondrites. However, most geochemists dismissed the differences as probable analytical error. This had some justification, since chemists had experienced great difficulty in separating the elements by conventional techniques. In his explanation of the principles of geochemistry, Goldschmidt (1937) had pointed out the importance of ionic radii to the geochemical distribution of the elements. The implications of this with respect to fractionation of the rare earths in rocks were only realized when the advent of sensitive analytical techniques, such as neutron activation, produced data which proved that a major fractionation of these elements had occurred.

Modern thought on rare earth geochemistry dates from a paper by Taylor (1962), in which he examined data by Schmidt et al. (1960) on chondrites, and by Sahama (1945), Garilova and Turanskaya (1968) and Graf (1960) on various crustal rocks. Taylor concluded that the differences between the data of Noddack and Minami were real, and he

decided that although the rare earth distribution for the whole earth was probably similar to that of chondrites, an upward concentration of the light rare earths had enriched the crust in these elements. He attributed this to a crystal chemical effect, due to the differences in ionic radii. The next major advance was made when Masuda (1962) and Coryell et al. (1963) suggested normalizing rare earth abundances to those of chondritic meteorites in order to make comparisons of abundance data. This removed the saw tooth effect of the Oddo-Harkins rule (even Z abundances > odd Z abundances), and resulted in smooth distribution patterns when chondrite normalized abundances were plotted versus atomic numbers or ionic radii.

The credit for suggesting that rare earth abundances in sediments are typical of the upper continental crust is due to Goldschmidt (1938). He considered that the mixing effect of weathering processes should result in a constant rare earth distribution for nearly all sediments. Later work by Ronov et al. (1972) has shown that Goldschmidt overestimated the degree of homogeneity of the rare earths in sediments. Sediments show differences in their rare earth distribution that reflect differences in both provenance and sedimentary rock type, but these differences are small when compared to the range in distribution shown by igneous rocks. Thus, sedimentary rocks are still considered as the best first approximation to the composition of the upper continental crust with respect to rare earth distribution. It should be said that this applies only to relative distribution and not to absolute abundances. The absolute abundances of the rare earths can exhibit wide variations between the different types of sedimentary rocks, but the relative abundances between the rare earth elements themselves show only small variations. Haskin et al. (1966) have proposed that the rare earth abundances in a composite of Palaeozoic

North American shales be taken as representative of the upper continental crust. In recent years it has become popular to normalize rare earth abundances in sedimentary rocks to the North American shales rather than to chondrites. Chondrite normalized plots allow comparison to the presumed upper mantle distribution, while shale normalized plots allow comparison to the upper crustal distribution.

Haskin and Gehl (1962) determined rare earth abundances in ten sedimentary rocks, and noted that the three Precambrian sediments all had anomalous distribution patterns. They suggested that this could be due to either selective leaching or to a lesser degree of homogeneity in the Precambrian crust. This came at a time of renewed interest in the subject of chemical evolution of the continental crust. A case for change and growth of the continental crust was made by Engel (1963) and Hurley et al. (1962), while the opposing view was put forward by Patterson and Tatsumoto (1964) and Condie (1967). The latter group held that the continents had achieved their present size and composition prior to about 3000 million years ago, and had changed very little since that time.

Balashov and Goryainov (1966) determined rare earth distributions in Lower Proterozoic metamorphic rocks, and observed that they were characterized by lower La/Yb ratios and much lower total rare earth contents than the North American shales. They attributed this to a gradual change from mafic to felsic magmatism through time. Felsic rocks have a tendency to be more highly enriched in the light rare earths and to have a higher total rare earth abundance than mafic rocks (Towell et al., 1965). Ronov et al. (1967) reported that they could detect no change in rare earth distribution patterns in sediments over the past 1500 million years. They postulated that Archaean sediments would show a distinctly different pattern due

to the mafic character which they believed Archaean sediments to have, and they suggested that a sharp change in rare earth distributions would occur at the boundary between the Archaean and the Lower Proterozoic. It has long been the contention of Ronov and his co-workers, that weathering products from granitic rocks only began to enter the sedimentary cycle in large amounts during the large scale granitization event at the end of the Archaean (Ronov and Migdisov, 1970). Schnetzler and Philpotts (1967) determined the rare earth distributions in five Precambrian sediments, with the expressed purpose of looking for signs of a gradual development of rare earth distribution through time. They reasoned that because the crust was enriched in the light rare earths, then the mantle might have become progressively depleted in these elements through time. According to this assumption, mantle derived rocks that were produced earlier in the earth's history would be expected to show a higher degree of enrichment in these elements than rocks produced in later periods. No significant difference was detected between the Precambrian sediments and younger sediments as represented by the North American shales. It was concluded that the rare earths might be concentrated into a small part of the mantle which serves as a source region for new crustal rocks, or that the lower crust may be depleted in the rare earths. Either of these possibilities would make an evolutionary change in rare earth distribution harder to detect. Using a similar approach, Goles (1968) failed to find any notable differences between Archaean and modern plutonic rocks. Haskin et al. (1968) reported that improved analytical data had shown the North American and European shales were deficient in Eu relative to the other rare earths when normalized to chondrites. In the same paper, preliminary results on Precambrian sediments

indicated they were enriched in Eu relative to the North American shales, and the degree of enrichment seemed to increase with age. In another important paper, Ronov et al. (1972) reported that sediments from geosynclines exhibited a different rare earth distribution to sediments of platform areas. This was thought to be due to a higher mafic volcanic component in the geosyncline, and to differences in conditions for weathering. The Eu enrichment in Lower Proterozoic and Archaean sediments reported by Haskin et al. (1968) was explained as being the result of a dominance of geosynclinal sedimentation with a high mafic component in the Early Precambrian. Wildeman and Haskin (1973) and Wildeman and Condie (1973) have confirmed the earlier report of anomalous Eu enrichment in ancient sediments with a study of rare earths in Lower Proterozoic and Archaean samples. Apart from the Eu enrichment and somewhat lower absolute rare earth abundances in the older rocks, they found the relative distribution patterns to be identical to that of the North American shales.

The effect of weathering during the sedimentary cycle on rare earth distribution was studied by Balashov et al. (1964). Weathering was not an important influence on the rare earth distribution in sediments formed under arid conditions, but in a humid environment the rare earths were concentrated in the clays and depleted in the sands.

La/Yb ratios were the same in clays, sands, and carbonates formed in an arid environment, but showed a progressive decrease from clays to sands to carbonates in a humid environment. In a later study (Ronov et al., 1967) they added the conclusion, "fractionation of the rare earths plays an insignificant role in the sedimentary cycle as a whole". Cullers et al. (1974) relied on weathering processes to explain differences in rare earth distribution between two formations of

metamorphosed sediments from Maine. They also implied that Eu depletions were due to weathering effects. Roaldset (1973) has interpreted the rare earth distribution of clays from the Numedal area, Norway as being strongly influenced by environmental factors.

Even though some local differences may be due to climatic changes or other environmental factors, it is reasonable to assume that an overall balance in rare earth abundances will be maintained. The abundances of the rare earths in sea water are very low (Wildeman and Haskin, 1965), so significant removal of the rare earths from continental areas does not seem likely. Much more work is needed before the role of weathering in distribution of the rare earth elements is known with any certainty.

The points on which previous investigators seem generally agreed can be summarized as follows.

1) Sediments have rather similar reltive rare earth distributions, although some variations occur.
2) Palaeozoic and younger sediments usually have a negative Eu anomaly relative to chondrites, while Early Precambrian sediments often have no Eu anomaly relative to chondrites.
3) The average rare earth abundances in sediments reflect the average rare earth abundances in the crystalline rocks of the upper crust.

Geological time scale

In order to avoid confusion, the geological time scale used in this thesis is presented in Fig. 1.2. The time scale recommended by Lambert (1971) is used for the Phanerozoic. Subdividing Precambrian

			Age to base (millions of years)
Cenozoic:	Quaternary:		
	Tertiary:	Pliocene	7
		Miocene	26
		Oligocene	38
		Eocene	54
		Palaeocene	65
Mesozoic:	Cretaceous		95
	Jurassic		200
	Triassic		240
Palaeozoic:	Permian		280
	Carboniferous		370
	Devonian		415
	Silurian		445
	Ordovician		515
	Cambrian		590
Upper Proterozoic:			1400
Middle Proterozoic:			1800
Lower Proterozoic:			2300
Archaean:			

Fig. 1.2 Geological time scale.

time presents a greater problem. Many different systems have been proposed for both world-wide (Vinogradov and Tugarinov, 1968) and Australian subdivisions (Dunn et al., 1966). Some terms such as "Archaean" and "Proterozoic" are in wide use, but there is no general agreement as to the age of the boundary between them (Rankama, 1971). The Precambrian subdivisions based on these terms shown in Fig. 1.2 were chosen because of their relevance to Australian stratigraphy (Dunn et al., 1966).

Chapter 2

Sample Selection

Introduction

The aim of sample selection was to obtain well preserved sedimentary rocks, and to cover the widest possible range in ages. Core samples were preferred, since they are less likely to have been altered by post depositional weathering than are rocks exposed in outcrop.

The ages of sedimentary formations listed in this chapter refer to the time of deposition. The time of deposition is known reasonably well for each of the sedimentary formations analyzed.

In this chapter the samples analyzed in this study are described. A brief description of the geology of each sampling area is given, and the major element chemistry of each sample is presented and discussed. The major element chemistry was provided by Dr. S.R. Taylor. The data was obtained with an X-ray fluorescence technique similar to that described by Norrish and Hutton (1969). Loss on ignition is the weight loss after heating to $1100^{o}C$.

A classification based on chemistry and petrography is given for each sample. The classification system used is that of Pettijohn (1957). Greywacke is the term used to denote a sandstone which contains abundant rock fragments and more than 15% clayey matrix. The term subgreywacke is used for rocks of the same type, but which contain less than 15% matrix. This distinction is strictly an arbitrary one, and it is recognized that these types of rocks grade into each other. The subgreywackes usually contain more SiO_2 and less Al_2O_3 than the greywackes, because of the lesser amount of clay minerals in subgreywackes. The term siltstone is used for rocks composed of mainly silt

sized particles (1/16 to 1/256 mm.), which contain only small amounts of matrix material. The term shale is used to denote similar rocks, but which contain more than about 25% clayey matrix and show fissility. More fundamental genetic differences are not meant to be implied by these terms as they are used here. Many of the rocks analyzed in this study have been subjected to low grade metamorphism, but this is not expected to have altered the rare earth distributions in any way. Hence, the equivalent metamorphic rock names are not used. A detailed description of sampling locations is given in the appendix. Fig. 2.1 shows the areas sampled.

The Eastern Goldfields Province

The oldest sediments analyzed in this study are those of the Kalgoorlie area of the Eastern Goldfields Province in the Yilgarn Block of Western Australia. The stratigraphy of the area has been discussed by Woodall (1965), Williams (1970), Travis et al. (1971), and Glikson (1971a). The region is composed of metamorphosed volcanics and sediments, which are enclosed by granites and granitic gneisses. The volcanics include ultra-mafic, mafic, and felsic rocks, and the sediments include greywackes, shales, and quartzites. The Province is considered to be Archaean in age (Compston and Arriens, 1968). It is part of what is usually referred to as a granite-greenstone terrain, and is similar to other Archaean granite-greenstone terrains in South Africa and North America (Anhaeusser, 1971a). These are among the oldest recognizable features on the earth's surface, and understanding them is a key factor in understanding the origin and evolution of the continents.

The Archaean samples used in this study were taken from the area around Kalgoorlie, W.A. The stratigraphy of the area between

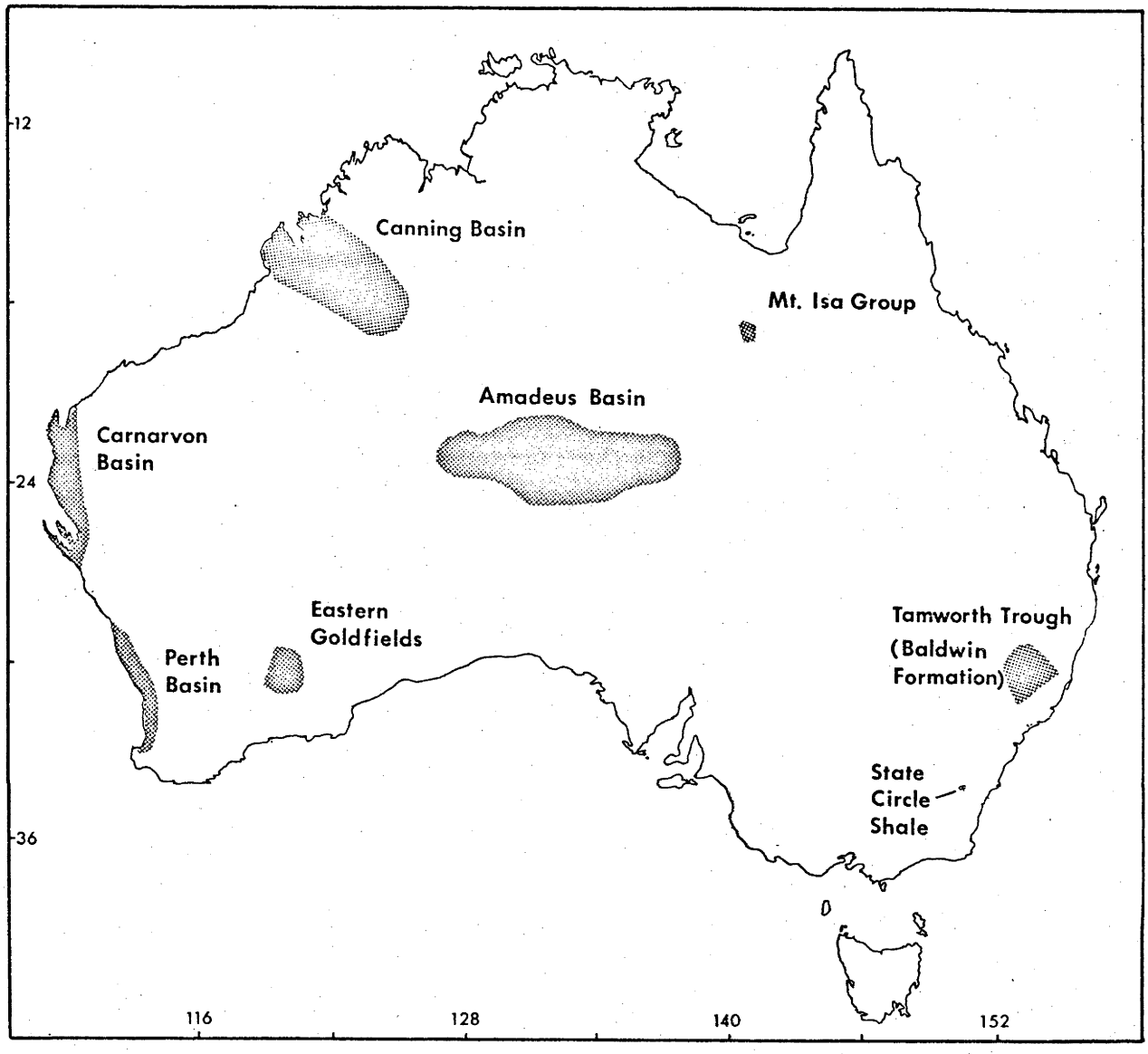

Fig. 2.1 Map of Australia showing the areas sampled. Shaded areas are the approximate areas of outcrop of the units sampled or related units.

Coolgardie and Kalgoorlie has been well documented by Glikson (1971a). Part of the sedimentary sequence in this area (the Mungari Beds) has been intruded by the Mungari Granite (Glikson 1971a). Rb-Sr dating of the Mungari Granite places a lower age limit of 2620 ± 20 million years on the Mungari Beds (Compston and Turek, 1973). Sedimentary units sampled include the Mungari Beds, the Black Flag Beds (Woodall, 1965), and unnamed units which probably correspond to the Association IV of Williams (1970). Ten Archaean samples from the Kalgoorlie area were analyzed. The major element chemistry of these samples is listed in Table 2.1. The samples were classified as follows. KH1 is a siliceous shale. KH21 is a high-alumina shale. KH30 is a dolomitic shale. KH32 and KH37 are shales, and both contain a very high silt content. KH36 is a subgreywacke. KH38 is an iron rich shale, and KH47 is a potassic shale. KH41 is a siliceous siltstone. KH44 is a greywacke. Most of the shales show enough recrystallization and fissility to be termed argillites or slates. Although many of the shales are nearly black in colour, they are probably not carbonaceous shales as defined by Pettijohn (1957).

Mount Isa Group

Middle Proterozoic sediments were obtained from the Mt. Isa Group in Northwestern Queensland. The geology of the area has been described by Bennett (1965). The Mt. Isa Group is a thick sequence of siltstones, shales, and bedded carbonates. The sequence is overlain by younger volcanics of uncertain age. A thick sequence of volcanics and sediments lie under the Mt. Isa Group, and they in turn overlie and are intruded by granites. The geochronology of the granites has been summarized by Compston and Arriens (1968). The most recent study of the geochronology of the area by the Bureau of Mineral Resources indicates a deposition age of 1400 - 1550 million years (Page and Derrick, 1973).

Table 2.1 Major element chemistry of Archaean sediments from the Kalgoorlie area

	KH1	KH21	KH30	KH32	KH36	KH37	KH38	KH41	KH44	KH47
SiO_2	85.50	66.75	39.14	74.63	75.14	66.96	54.36	78.00	64.57	61.28
TiO_2	0.61	0.80	0.32	0.37	0.55	0.50	0.40	0.24	0.48	0.75
Al_2O_3	6.49	22.13	8.97	16.02	14.61	12.09	11.10	14.35	12.76	17.59
Fe_2O_3*	2.16	0.78	8.21	1.10	2.42	9.41	16.04	9.98	8.01	1.43
MgO	0.57	0.47	8.39	0.38	1.03	0.66	1.23	0.67	2.69	0.58
CaO	0.19	0.06	12.06	0.08	0.03	0.10	0.50	0.03	1.18	1.34
Na_2O	0.24	0.64	0.58	1.12	0.26	0.32	0.44	0.09	1.65	2.43
K_2O	1.57	4.29	0.62	3.48	3.84	3.25	2.18	3.07	1.95	6.50
MnO	-	0.01	0.42	-	0.01	0.01	0.02	-	0.02	0.01
P_2O_5	0.04	0.05	0.08	0.11	0.03	0.05	0.07	0.01	0.05	0.02
Loss on ignition	2.20	3.31	20.80	3.46	2.05	7.17	14.64	2.55	6.23	7.00
Total	99.57	99.29	99.59	100.75	99.97	100.52	100.98	99.99	99.59	98.93

*Total Fe as Fe_2O_3

The stratigraphy of the Mt. Isa Group from youngest to oldest formation is: Magazine Shale; Spear Siltstone, Kennedy Siltstone; Urquhart Shale; Native Bee Siltstone; Breakaway Shale; and Moondarra Siltstone. The group has enormous economic importance, since it is one of the world's largest known deposits of base metals. The Urquhart Shale contains all the known economic mineralization, but the whole group has been closely studied by mining company geologists. A geochemical study of the group has been made by Smith and Walker (1971).

One sample each of the Magazine Shale, Spear-Kennedy Siltstone, Native Bee Siltstone, and Breakaway Shale was analyzed in this study. The samples were supplied by Mt. Isa Mines Ltd., and were all core samples taken from depths ranging from 340 to 2900 ft. The major element chemistry of these samples is listed in Table 2.2. Examination of thin sections of these samples, and consideration of their major element chemistry leads to the following classifications. MI1 is a siliceous shale. MI2 is a dolomitic siltstone. MI4 and MI5 are shales. MI1 and in particular MI4 have high Na_2O/K_2O ratios, which is sometimes considered as evidence for a low degree of chemical maturity.

Amadeus Basin

Upper Proterozoic sediments from the Amadeus Basin, Central Australia were chosen to complete the suite of Precambrian samples. The geology of the area has been described by Wells et al. (1967). The crystalline rocks of the Arunta complex are overlain by a thick sedimentary sequence in the Amadeus Basin. The age of the rocks of the Arunta complex is uncertain, but is probably at least 1600 million years as deduced from a summary of age data on intruding granites (Compston and Arriens, 1968). The real age is probably much older than

Table 2.2 Major element chemistry of Middle Proterozoic sediments of the Mt. Isa Group

	MI1	MI2	MI4	MI5
SiO_2	70.97	56.15	69.80	65.86
TiO_2	0.45	0.26	0.49	0.75
Al_2O_3	13.84	6.91	13.33	14.70
Fe_2O_3*	4.20	2.05	3.98	6.51
MgO	2.46	4.92	1.48	2.46
CaO	0.34	12.06	0.80	0.48
Na_2O	1.17	3.38	1.70	0.40
K_2O	3.60	0.75	2.88	3.69
MnO	0.04	0.35	0.06	0.04
P_2O_5	0.21	0.14	0.18	0.30
Loss on ignition	3.38	13.90	5.70	4.29
Total	100.66	100.87	100.40	99.48

*Total Fe as Fe_2O_3

that, but no reliable older age limit has been set. The stratigraphy of the Precambrian sedimentary sequence from oldest to youngest rocks is: Heavitree Quartzite; Bitter Springs Formation; Areyonga Formation; and Pertatataka Formation. Age data on the succession has been summarized by Compston and Arriens (1968). Shales of the Pertatataka Formation cored from the Ooraminna No. 1 well have been dated by Rb-Sr at 790 million years. The same age was obtained for cores of the Pertatataka Formation from the Mt. Charlotte No. 1 well. Other shales from uncertain but perhaps higher stratigraphic positions from cores taken from various other wells have given isochrons of about 600 million years. Compston and Arriens (1968) regarded all of these as minimum ages of deposition, but concluded that these shales were not much older than 800 million years. Wells et al. (1967) quoted an unpublished Rb-Sr age of 1170 million years for shales of the Bitter Springs Formation. Thus, it seems that no very precise dates for deposition of these sediments is available, although for the purposes of this study an age of about 850 million years will be assumed. The Pertaoorrta Group, which overlies the Pertatataka Formation, is considered to be Lower Cambrian by Wells et al. (1967).

Wells et al. (1967) have suggested that the provenance rocks for the Areyonga and Pertatataka Formations were older basement rocks uplifted during later tectonism. This means that a very large difference may exist between the age of the source rocks and the time of deposition of the sediments. Thus, the ages of the Mt. Isa and Amadeus Basin sediments with respect to source rocks may be nearly the same.

Samples from the Amadeus Basin used in this study were taken from cores from the Ooraminna No. 1 well. The cores were furnished by the Bureau of Mineral Resources, Canberra. The Upper Proterozoic Bitter Springs, Areyonga, and Pertatataka Formations, and the Arumbera sandstone of the Lower Cambrian Pertaoorrta Group were represented in

a total of 9 samples. Table 2.3 lists the major element chemistry of these samples. A014 is a spilite (an altered igneous rock) which was intersected in the Bitter Springs Formation by the Ooraminna No. 1 well. Examination of thin sections and consideration of the chemistry of these samples leads to their classification as follows. A03, A04, and A05 are either subgreywackes or arkoses. Their high MgO contents favour their classification as subgreywackes. A06, A07, A09, A010 and A012 are shales. The amount of sand sized detritus decreases with the depth from which these samples were taken in the well.

State Circle Shale

A suite of 7 samples from the State Circle Shale, Canberra were analyzed in this study. The geology of the area has been described by Öpik (1958). The samples were taken from an Australian National University borehole on Camp Hill. The hole reached a total depth of 211 feet. The upper 100 feet of core was oxidized and iron stained, so the samples were taken from the lower 40 feet of core. Samples of the shale from this borehole were dated by Rb-Sr isochron at 445 $\pm$ 7 million years by Bofinger et al. (1970). This places the age of deposition in the Lower Silurian. The samples have been subject to only a very low degree of metamorphism.

Table 2.4 lists the major element chemistry of these samples. The samples show very little variation in major element chemistry. Examination of thin sections reveals that although the samples are shales, they contain a very high percentage of silt sized particles. This probably accounts for their high SiO_2 contents and high SiO_2/Al_2O_3 ratios.

Baldwin Formation

Chappell (1968) has made an intensive study of the chemistry and petrography of the greywackes of the Baldwin Formation, Tamworth-

Table 2.3 Major element chemistry of Upper Proterozoic and Palaeozoic sediments from the Amadeus Basin

	A03	A04	A05	A06	A07	A09	A010	A012	A014
SiO_2	68.25	77.92	82.48	61.13	61.75	65.83	62.97	56.56	48.88
TiO_2	0.56	0.57	0.40	0.65	0.72	0.72	0.80	0.79	1.77
Al_2O_3	7.85	7.93	6.02	14.54	14.50	14.57	15.84	20.66	13.60
Fe_2O_3*	3.78	1.81	2.43	5.80	7.81	6.79	7.08	5.75	13.80
MgO	4.03	2.45	1.38	3.48	2.60	2.29	1.92	3.13	7.83
CaO	4.16	2.04	1.28	2.45	1.22	0.40	0.25	0.13	8.25
Na_2O	0.41	0.64	0.70	0.93	0.80	0.98	0.94	0.82	2.82
K_2O	3.17	3.48	3.32	4.34	4.24	3.66	4.16	8.41	1.51
MnO	0.07	0.03	0.02	0.12	0.12	0.11	0.08	0.02	0.17
P_2O_5	0.11	0.12	0.07	0.06	0.05	0.08	0.11	0.05	0.15
Loss on ignition	7.62	4.15	2.34	6.24	6.66	4.81	5.57	3.86	1.83
Total	100.01	101.14	100.44	99.74	100.47	100.24	99.72	100.18	100.62

*Total Fe as Fe_2O_3

Table 2.4 Major element chemistry of Palaeozoic sediments from the State Circle Shale

	SC1	SC2	SC3	SC4	SC5	SC7	SC8
SiO_2	65.07	65.34	67.03	64.65	65.34	65.58	65.58
TiO_2	0.70	0.71	0.68	0.70	0.72	0.69	0.72
Al_2O_3	16.34	16.50	15.32	16.52	17.00	16.16	16.51
Fe_2O_3*	6.55	6.25	6.51	6.52	5.99	7.17	6.32
MgO	2.77	2.63	2.67	2.81	2.68	2.80	2.63
CaO	0.24	0.23	0.22	0.24	0.22	0.23	0.21
Na_2O	0.46	0.36	0.45	0.30	0.25	0.37	0.64
K_2O	4.01	4.23	3.69	4.16	4.45	3.85	4.09
MnO	0.41	0.25	0.39	0.40	0.25	0.20	0.22
P_2O_5	0.14	0.15	0.15	0.16	0.15	0.14	0.14
Loss on ignition	3.20	3.18	3.09	3.28	3.26	3.22	3.12
Total	99.89	99.83	100.20	99.74	100.31	100.41	100.18

*Total Fe as Fe_2O_3

Barraba district, New South Wales. It was concluded that they were volcanic greywackes, which were formed by fast erosion and deposition of andesites. These greywackes are Upper Devonian in age. They were included in this study in order to provide a sample which was formed from a purely volcanic source.

Table 2.5 lists the major element chemistry of the seven samples from the Baldwin Formation used in this study. They were obtained from Dr. B.W. Chappell, and are the same specimens used in his study. Examination of thin sections of these samples clearly establishes their classification as volcanic greywackes.

Canning Basin

Seven samples of Palaeozoic sediments were taken from cores of the Langoora No. 1 well in the Canning Basin, Western Australia. The formations sampled include: Poole (Permian); Grant (Permian); and Laurel (Lower Carboniferous). The detailed stratigraphy is reported by Gardner (1963). The samples were taken from depths ranging from 1900 to 5100 feet. The sedimentary sequence lies over a Precambrian basement schist, which was encountered at 5240 feet by the Langoora No. 1 well. The samples were obtained from the Bureau of Mineral Resources, Canberra.

Table 2.6 lists the major element chemistry of these samples. Classification of the samples by examination of thin sections and major element chemistry is as follows. PL1 and PL6, are shales, and PL7 is a siltstone. PL3, PL4 and PL5 are orthoquartzites, and PL8 is an arenaceous limestone.

Perth Basin

Palaeozoic and Mesozoic sediments were obtained from cores of the Wool Mulla No. 1 well, Perth Basin, Western Australia. The stratigraphy is described by Pudowskis (1963). The formations sampled were: Woodada (Middle Triassic); Kockatea Shale (Lower Triassic); and

Table 2.5 Major element chemistry of Palaeozoic sediments from the Baldwin Formation

	M216	M277	M282	M283	M284	M285	B10
SiO_2	54.13	54.04	55.09	52.08	56.98	58.39	53.55
TiO_2	1.24	1.33	1.18	1.16	0.98	0.79	1.40
Al_2O_3	14.69	15.53	16.35	14.13	16.41	16.82	15.39
Fe_2O_3*	11.34	11.96	10.25	10.31	7.74	6.59	12.19
MgO	5.90	3.89	3.79	3.61	2.73	2.36	4.44
CaO	5.34	5.01	3.71	8.84	4.70	5.30	4.14
Na_2O	4.19	4.40	5.26	4.07	6.26	5.51	4.62
K_2O	0.81	0.53	0.96	0.30	0.72	0.71	0.94
MnO	0.13	0.18	0.14	0.22	0.22	0.11	0.18
P_2O_5	0.20	0.23	0.26	0.25	0.19	0.14	0.24
Loss on ignition	3.94	3.50	3.35	5.74	3.09	2.83	3.57
Total	101.91	100.60	100.34	100.71	100.02	99.55	100.66

*Total Fe as Fe_2O_3

Table 2.6 Major element chemistry of Palaeozoic sediments from the Canning Basin

	PL1	PL3	PL4	PL5	PL6	PL7	PL8
SiO_2	63.51	95.16	96.72	91.92	61.08	66.81	30.46
TiO_2	0.73	0.11	0.06	0.08	0.68	0.79	0.22
Al_2O_3	18.76	3.33	1.84	1.22	15.67	16.59	0.80
Fe_2O_3 *	5.81	0.16	0.21	0.98	4.93	5.41	0.43
MgO	1.53	0.18	0.21	0.20	1.86	1.79	0.80
CaO	0.37	0.07	0.04	3.08	4.73	0.62	37.94
Na_2O	0.17	0.06	0.05	0.04	0.43	0.53	0.01
K_2O	4.09	1.25	0.84	0.43	3.47	3.58	0.18
MnO	0.04	-	-	0.12	0.05	0.03	0.01
P_2O_5	0.08	0.01	0.02	0.01	0.10	0.11	0.05
Loss on ignition	4.34	0.42	0.20	2.63	7.31	4.27	30.00
Total	99.43	100.75	100.19	100.71	100.31	100.53	100.90

* Total Fe as Fe_2O_3

Carynginia (Permian). The sediments overlie a basement of Precambrian metamorphic rocks. Seven samples from this well were analysed.

Table 2.7 lsits their major element chemistry. A classification of these samples was made on the basis of an examination of thin section and their major element chemistry. PW4, PW5, and PW7 are normal shales. PW2 is an arkose. PW8, PW9, and PW10 are subgreywackes.

Carnarvon Basin

Cenozoic and Mesozoic sediments were obtained from the Learmonth No. 2 well in the Carnarvon Basin, Western Australia. The stratigraphy of the Carnarvon Basin was described by Condon (1968), and the detailed stratigraphy at the well site by Pudowskis (1964). Four core samples were obtained from the Bureau of Mineral Resources, Canberra of the Giralia Calearenite (Eocene); and the Wogatti Sandstone (Lower Cretaceous).

The major element chemistry of these samples is listed in Table 2.8. Examination of thin sections and major element chemistry leads to the following classifications. CL1 is a calcarenaceous sandstone containing bright green glauconite. CL2 is a siliceous siltstone containing a large amount of amorphous silica. CL3 is a silty mudstone, with a very high percentage of silt and sand sized detrital quartz. CL4 is an iron rich mudstone containing pisolitic siderite.

Summary

All of the samples are listed in Table 2.9 according to their classification. Of the 54 samples, shales are the most abundant (28) followed by greywackes (8), subgreywackes (7), siltstones (3), quartzites (3), mudstones (2), arkoses (1), carbonates (1), and calcarenaceous sandstones (1).

Table 2.7 Major element chemistry of Palaeozoic and Mesozoic sediments from the Perth Basin

	PW2	PW4	PW5	PW7	PW8	PW9	PW10
SiO_2	83.62	57.86	55.34	59.56	72.00	76.78	69.28
TiO_2	0.42	0.99	0.96	0.91	0.45	0.74	0.96
Al_2O_3	6.89	22.46	22.08	19.17	9.85	11.67	15.39
Fe_2O_3*	4.57	7.89	8.82	10.41	4.76	3.06	3.89
MgO	0.43	1.80	1.68	1.99	2.13	0.89	1.00
CaO	0.19	0.40	0.53	0.53	2.80	0.78	0.53
Na_2O_3	0.14	0.90	0.88	1.68	0.85	1.12	0.82
K_2O	2.03	3.99	3.20	2.69	1.61	2.33	3.40
MnO	0.05	0.08	0.15	0.11	0.07	0.04	0.02
P_2O_5	0.03	0.19	0.21	0.15	0.07	0.05	0.12
Loss on ignition	1.13	4.05	5.50	3.58	5.55	3.01	3.72
Total	99.50	100.61	99.35	100.78	100.14	100.47	99.13

* Total Fe as Fe_2O_3

Table 2.8 Major element chemistry of Mesozoic and Cenozoic sediments from the Carnarvon Basin

	CL1	CL2	CL3	CL4
SiO_2	50.52	89.29	64.47	49.76
TiO_2	0.26	0.41	1.39	0.97
Al_2O_3	2.82	6.95	25.88	20.35
Fe_2O_3*	3.64	0.41	1.52	20.66
MgO	4.61	0.16	0.13	0.64
CaO	18.31	0.07	0.03	0.33
Na_2O	1.05	0.81	0.14	0.10
K_2O	1.43	0.40	0.23	0.31
MnO	0.01	-	-	0.16
P_2O_5	0.12	0.06	0.03	0.03
Loss on ignition	18.87	1.65	6.38	7.08
Total	101.64	100.21	100.20	100.39

*Total Fe as Fe_2O_3

Table 2.9 Ages and classifications of the sedimentary rock samples.

Sample	Rock Type	Age
KH1	shale	Archaean
KH21	shale	"
KH30	shale	"
KH32	shale	"
KH36	subgreywacke	"
KH37	shale	"
KH38	shale	"
KH41	siltstone	"
KH44	greywacke	"
KH47	shale	"
MI1	shale	Middle Proterozoic
MI2	siltstone	"
MI4	shale	"
MI5	shale	"
A012	shale	Upper Proterozoic
A010	shale	"
A09	shale	"
A07	shale	"
A06	shale	"
A05	subgreywacke	Cambrian
A04	subgreywacke	"
A03	subgreywacke	"
SC1	shale	Silurian
SC2	shale	"
SC3	shale	"
SC4	shale	"
SC5	shale	"
SC7	shale	"

Table 2.9 (continued)

Sample	Rock Type	Age
SC8	shale	Silurian
M216	greywacke	Devonian
M277	greywacke	"
M282	greywacke	"
M283	greywacke	"
M284	greywacke	"
B10	greywacke	"
PL8	arenaceous limestone	Carboniferous
PL7	siltstone	"
PL6	shale	"
PL5	orthoquartzite	Permian
PL4	orthoquartzite	"
PL3	orthoquartzite	"
PL1	shale	"
PW10	subgreywacke	"
PW9	subgreywacke	"
PW8	subgreywacke	"
PW7	shale	Triassic
PW5	shale	"
PW4	shale	"
PW2	arkose	"
CL4	mudstone	Jurassic
CL3	mudstone	"
CL2	siltstone	"
CL1	calcarenaceous sandstone	Eocene

CHAPTER 3

Analytical Methods

Sample crushing

All grinding and mixing operations were done in an agate ball mill. The agate ball and vial were treated with a dilute HF solution to remove all traces of rare earth contamination introduced by polishing operations during their manufacture. This is not a trivial matter, since the manufacturers of agate grinding implements have the undesirable practice of using rare earth oxides as a polishing compound. The samples were ground for at least 20 minutes (double the normal time), in order to crush the very hard resistate minerals (e.g. zircon) which are common in sediments. This is usually adequate to reduce the particle size to less than 200 mesh.

Mass spectrography

The samples were analysed with an AEI MS7 spark source mass spectrograph. The method has been described by Taylor (1965, 1971), but some recent modifications have been made. Quantitative abundance data were obtained for: Th, U, Hf, Yb, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La, Ba, Cs and Y. The method utilizes the rare earth element Lu as an internal standard, so its abundance can not be directly determined. The rare earth Tm suffers a serious interference from a multiple carbon molecule, so its abundance is also not determined. The abundance of both Lu and Tm may be estimated from the rare earth pattern. The rare earth Pm has no stable isotopes, and so it is not detected.

The sample is mixed 1:1 with a graphite mix containing 50 ppm Lu as Lu_2O_3. Electrodes are then prepared inside polyethylene slugs using a steel die and hydraulic press. The electrodes are placed in the source of the mass spectrograph, and subjected to a high voltage spark.

The ion beam produced is collected on an Ilford Q-2 photographic plate. Up to 16 graded exposures are spaced across each plate. The densities of mass lines are determined with a micro-photodensitometer. The photoplates are calibrated by plotting the densities of lines for isotope pairs against their known abundance ratios. The slope of a line drawn through these points is used as the plate response to incident ions. The density of a mass line is plotted on a vertical Seidel scale, and a line with a slope determined as above is drawn through this point. The intercept of this line with a horizontal log scale is used as the intensity of this line. The ratio of the intensity of a mass line to the intensity of the internal standard line on the same exposure is directly related to element abundance. Calibration of this ratio to elemental abundance is achieved with rock standards such as W-1, G-1, BCR-1 and AGV-1.

The rare earth Lu is an ideal internal standard for the other rare earths. ^{176}Lu, which is used as the internal standard for high exposure levels, has interference from ^{176}Yb and ^{176}Hf. This is corrected for by measuring the ^{171}Yb and ^{178}Hf lines, and converting these to ^{176}Yb and ^{176}Hf using the known isotope abundance ratios. These are subtracted from the total intensity of the 176 line to obtain the corrected ^{176}Lu intensity. The natural Lu content is corrected for by estimating the abundance of Lu from those of Yb and Er, and then, the calculations for all lines are repeated using the corrected internal standard intensity. The nuclide lines used for Tb, Gd, Dy and Yb suffer small interferences from Ba, La, Ce and Nd carbides and oxides. The interferences are only detectable when light rare earth and/or Ba abundances are very high, and heavy rare earth abundances are very low. Empirical corrections can be made on these lines based on the measured abundances of the interfering elements. The corrections are necessary in only a few cases, since the normal level of interference on these lines is much less than the

precision of the method.

Accuracy and precision of the method are dependent upon the total number of exposures used to calculate the abundance of each element, as well as other factors. For this study two photoplates were exposed for each sample, each with about 15 exposures, and determinations for many elements were based on more than one isotope. This resulted in the measured abundance of each element being based on 8-20 determinations. The precision obtained for all elements was about $\pm$3% expressed as standard error. Results obtained by this technique on standard rocks and lunar samples have been compared with results obtained on the same samples by other well recognized methods. Table 3.1 shows such a comparison made by Taylor et al. (1973) for a lunar soil sample. This and other comparisons indicate the accuracy of the method is about $\pm$ 10%.

All data reduction was done with a Univac 1108 computer. The computer program was described by Gorton (1974).

Table 3.1 Comparison of trace element data for Apollo 15 lunar soil sample 15471.

Element	MS7[1] (ppm)	Other (ppm)	Method	Reference
Th	2.38	2.28	ID	2
U	0.61	0.62	ID	2
Hf	5.5	4.5	NA	3
Cs	0.18	0.12	NA	4
La	14.7	13.9	NA	5
Ce	38.4	34.4	NA	5
Nd	24.3	26	NA	5
Sm	6.6	7.1	NA	5
Eu	1.17	1.05	NA	5
Gd	8.2	8.7	NA	5
Tb	1.3	1.5	NA	5
Dy	8.8	10	NA	5
Ho	2.1	2.1	NA	5
Er	5.8	5.4	NA	5
Yb	5.8	5.1	NA	5
Y	54	52	XRF	6

1 Taylor et al., 1973

2 Silver, 1972

3 Wänke et al., 1972

4 Morgan et al., 1972

5 Helmke and Haskin, 1972

6 LSPET, 1972

Chapter 4

Experimental Results

Introduction

A total of 53 sedimentary rocks were analyzed for Th, U, Hf, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Ba, Cs and Y. Major element chemistry and the rock classification of each of these samples were reported in Chapter 2. In this chapter the trace element data are reported. All results are reported on a volatile free basis. The rare earth data are presented normalized to the abundances of those elements in both chondrites and the North American Shale Composite (NASC). Chondrites are assumed to represent the primordial solar abundances of these elements, and perhaps their abundances in the earth as a whole. The rare earth abundances in the NASC are frequently used as an approximation to those in the upper continental crust. The NASC is enriched in the light rare earths relative to the heavy rare earths when compared to chondritic abundances. The NASC is also depleted in Eu relative to the adjacent rare earths (Sm and GD). The values used for rare earth abundances in chondrites and the NASC are listed in Table 4.1. The expression Eu/Eu^* is the ratio of the measured Eu abundance to that which is calculated for a smooth chondrite normalized rare earth pattern by interpolation between Gd and Sm. Thus, it is a measure of the depletion or enrichment of Eu relative to the adjacent rare earths in a chondrite normalized distribution pattern. Values of Eu/Eu^* must differ from unity by an amount greater than normal analytical variation to be considered significant Eu anomalies. For the data presented here, values of Eu/Eu^* outside the range 0.90 - 1.10 will be considered as significant anomalies. The term ΣLREE/ΣHREE is the ratio of the sum of the abundances of La-Sm to the sum of the abundances of Gd-Yb. Elements not directly measured (Tm and Lu) were excluded from the summation. This term is used as a measure of the degree to which the light and heavy rare earths have been fractionated relative to each other. For example, chondrites have a

Table 4.1 Rare earth abundances used for normalizing. Chondrite data were compiled from Haskin et al. (1966), Haskin et al. (1968) and Hubbard and Gast (1971). Abundances in the North American shale composite are from Haskin et al. (1968).

	Chondrites (ppm)	NASC (ppm)
La	0.30	32
Ce	0.84	70
Pr	0.12	7.9
Nd	0.58	31
Sm	0.21	5.7
Eu	0.074	1.24
Gd	0.30	5.2
Tb	0.049	0.85
Dy	0.31	5.0
Ho	0.073	1.04
Er	0.21	3.4
Yb	0.20	3.1

ΣLREE/ΣHREE ratio of about 1.8, and for the NASC it is 8.0.

Eastern Goldfields Province

The trace element abundances in the Archaean sediments from the Kalgoorlie area are listed in Table 4.2, along with some important elemental ratios. Figs. 4.1, 4.2, and 4.3 present chondrite and shale normalized rare earth patterns for these samples. Seven of the samples show significant enrichments of Eu relative to chondrites. The remaining three samples do not have significant enrichments or depletions in Eu relative to chondrites. All of these samples are significantly enriched in Eu relative to the NASC. KH41 has a very low total rare earth abundance (ΣREE) of only 9 ppm, and a low ΣLREE/ΣHREE of 3.5. The relative rare earth patterns of KH1, KH36, KH37, KH38, KH44, and KH47 are all similar to each other. They are depleted in the lightest rare earths relative to the NASC, with ΣLREE/ΣHREE in the range 5.4 - 6.7. ΣREE range from 53 ppm to 110 ppm, which are considerably lower than ΣREE for the NASC (166 ppm). KH21, KH30, and KH32 are depleted in the heaviest rare earths relative to the NASC. ΣLREE/ΣHREE for these samples ranges from 11 to 18, and ΣREE ranges from 91 ppm to 162 ppm. The Archaean sediments can thus be divided into two groups (excluding KH41) on the basis of ΣLREE/ΣHREE ratios.

Mt. Isa Group

Table 4.3 lists the trace element abundances for the Middle Proterozoic sediments from the Mt. Isa Group. Fig. 4.4 shows the chondrite and shale normalized rare earth patterns for these samples. All four samples show significant depletions in Eu relative to chondrites, but are nearly normal relative to the NASC. ΣLREE/ΣHREE ranges from 9.0 to 13, and ΣREE ranges from 117 ppm to 172 ppm. In most respects, the rare earth patterns of these sediments are similar to that of the NASC, as shown by their nearly flat shale normalized patterns in Fig. 4.4.

Table 4.2 Rare earths and other trace elements in Archaean sediments from the Eastern Goldfields Province.

	KH1	KH21	KH30	KH32	KH36	KH37	KH38	KH41	KH44	KH47
Th	3.0	16	5.2	5.6	3.3	4.3	6.9	9.7	6.3	4.1
U	1.5	2.0	23	1.2	1.2	1.3	1.9	1.5	1.6	0.97
Hf	2.9	3.7	1.6	2.6	2.3	2.2	4.1	2.2	2.8	3.3
Ba	180	1200	180	520	370	360	540	410	790	900
Cs	0.92	8.9	5.8	4.0	5.3	5.2	4.7	1.2	1.3	1.5
La	11	36	19	24	14	15	23	1.8	17	11
Ce	23	75	40	54	30	31	45	3.0	33	23
Pr	2.5	8.9	5.1	5.7	3.2	4.0	5.5	0.35	4.4	2.2
Nd	7.9	27	16	18	11	14	18	1.3	15	7.9
Sm	1.3	4.9	2.8	2.6	2.5	3.2	4.0	0.45	3.1	2.1
Eu	0.54	1.2	0.97	0.78	1.1	1.5	1.3	0.13	1.1	0.80
Gd	1.5	3.7	2.5	2.5	2.3	3.5	3.6	0.52	3.2	2.0
Tb	0.30	0.49	0.32	0.30	0.42	0.56	0.54	0.09	0.49	0.31
Dy	2.1	2.5	1.7	1.5	2.7	3.7	3.5	0.51	3.1	1.9
Ho	0.45	0.39	0.38	0.28	0.49	0.59	0.82	0.11	0.64	0.40
Er	1.3	1.0	1.2	0.67	1.6	1.9	2.5	0.32	1.8	1.3
Yb	1.5	0.44	1.1	0.68	1.5	2.0	2.5	0.37	1.6	1.3
Σ REE	53	162	91	111	71	81	110	9.0	84	54
Y	10	11	10	5.6	18	12	22	2.4	12	11
Σ REE+Y	63	173	101	117	89	93	132	11	96	65
Eu/Eu^*	1.30	0.91	1.22	1.03	1.52	1.51	1.10	0.95	1.18	1.29
La/Yb	7.3	82	17	35	9.3	7.5	9.2	4.9	11	8.5
La/Sm	8.5	7.3	6.8	9.2	5.6	4.7	5.8	4.0	5.5	5.2
La/Th	3.7	2.3	3.7	4.3	4.2	3.5	3.3	0.19	2.7	2.7
Th/U	2.0	8.0	0.23	4.3	2.8	3.3	3.6	6.5	3.9	4.2
ΣLREE/ ΣHREE	6.4	18	11	17	6.5	5.4	6.7	3.5	6.7	6.3

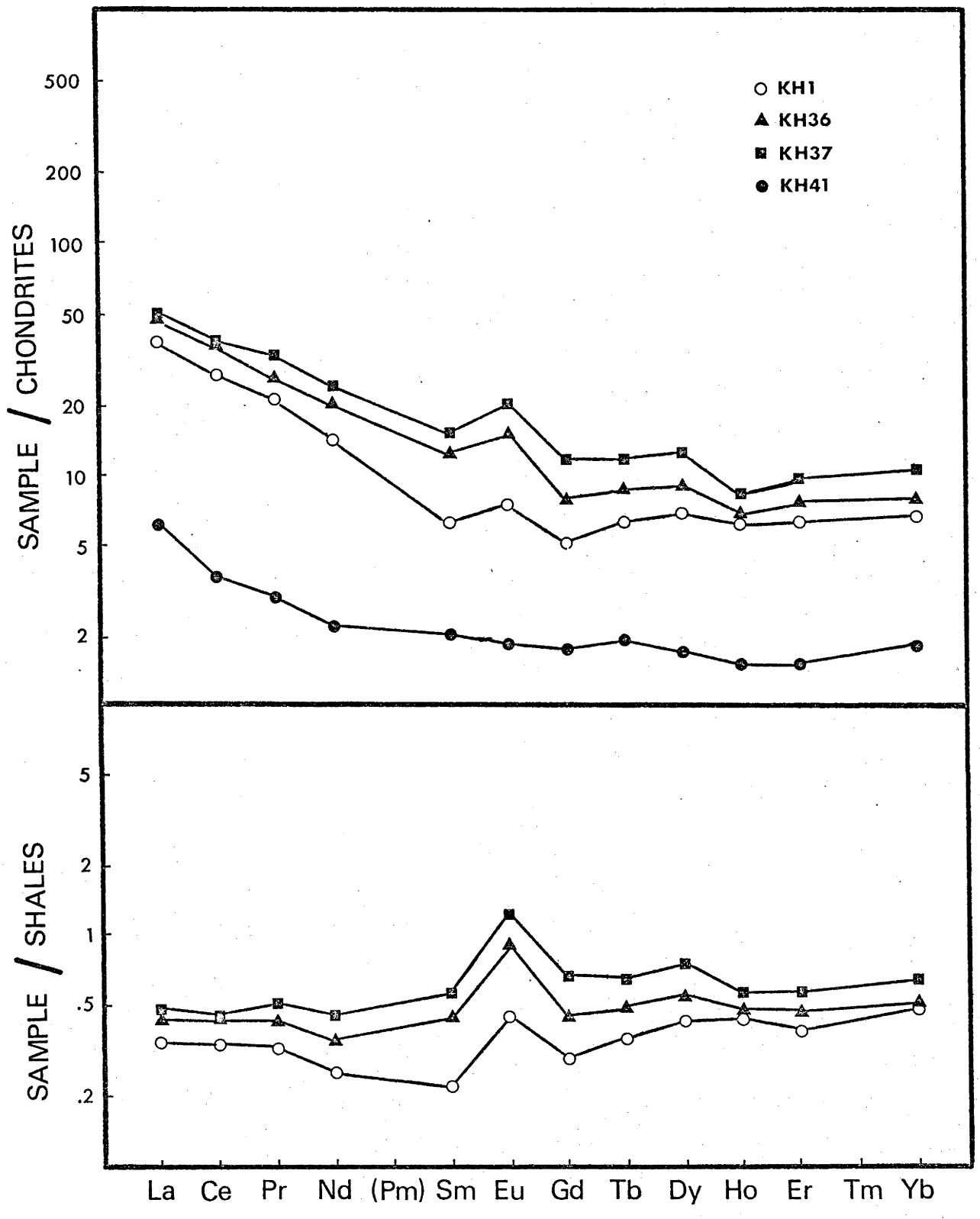

Fig. 4.1 Rare earth patterns for some Archaean sediments from the Kalgoorlie area.

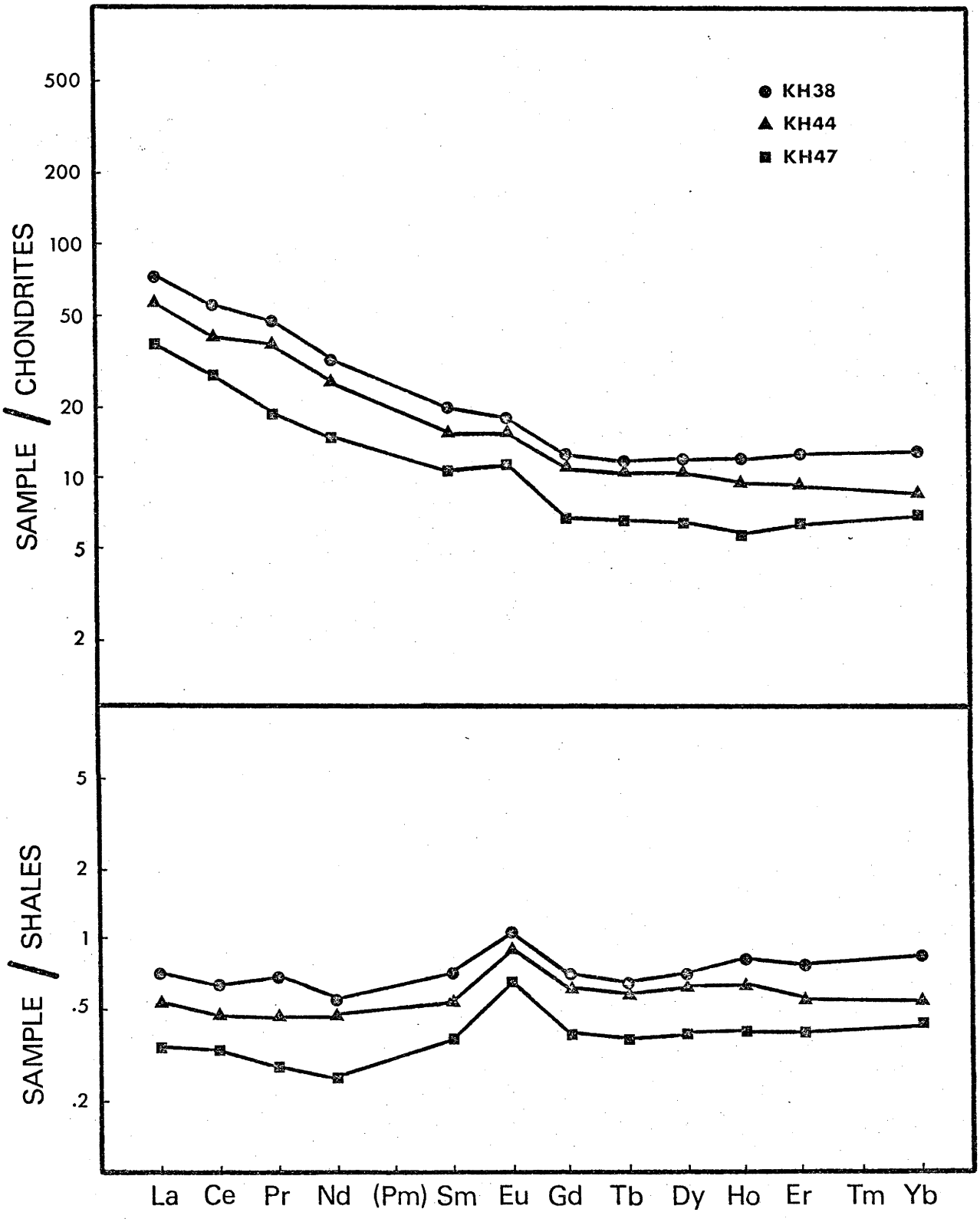

Fig. 4.2 Rare earth patterns for some Archaean sediments from the Kalgoorlie area.

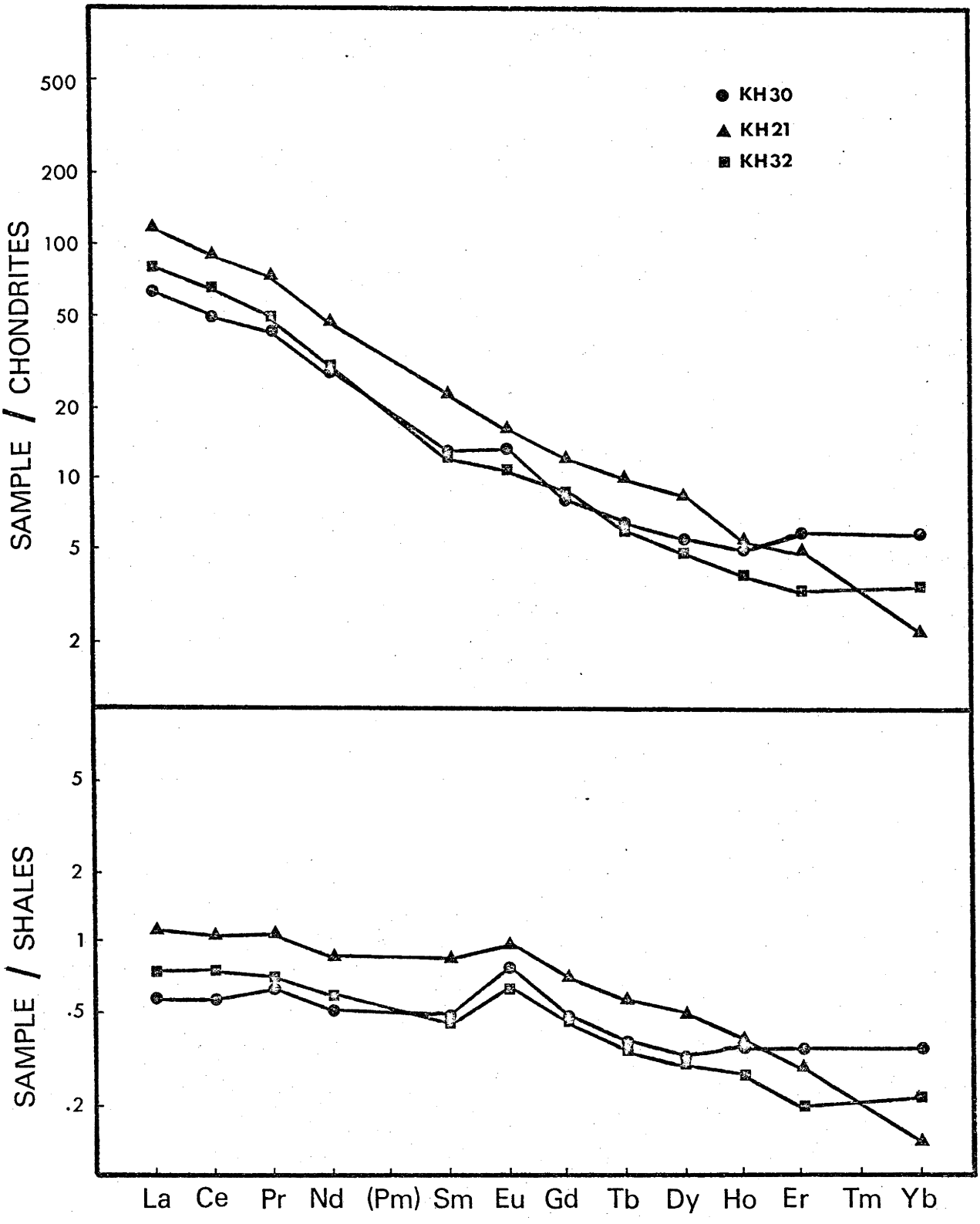

Fig. 4.3 Rare earth patterns for some Archaean sediments from the Kalgoorlie area.

Table 4.3 Rare earths and other trace elements in Middle Proterozoic sediments from the Mt. Isa Group

	MI1	MI2	MI4	MI5
Th	10	8.8	11	12
U	2.7	2.2	8.0	2.7
Hf	2.1	2.1	3.0	4.1
Ba	450	29	550	310
Cs	7.3	4.3	12	16
La	27	38	30	27
Ce	52	80	61	57
Pr	5.1	8.6	6.6	8.8
Nd	17	28	22	32
Sm	3.6	4.5	4.3	4.9
Eu	0.75	0.69	0.81	0.94
Gd	3.5	3.5	4.2	4.0
Tb	0.53	0.55	0.63	0.68
Dy	3.2	3.3	3.8	3.8
Ho	0.61	0.71	0.77	0.86
Er	1.7	2.0	2.0	2.3
Yb	1.7	2.1	2.0	2.4
Σ REE	117	172	138	145
Y	14	21	24	18
Σ REE+Y	131	193	162	163
Eu/Eu^*	0.69	0.57	0.62	0.70
La/Yb	16	18	15	11
La/Sm	7.5	8.4	6.9	5.5
La/Th	2.7	4.3	2.7	2.3
Th/U	3.7	4.0	1.4	4.4
ΣLREE/ ΣHREE	9.4	13	9.0	9.0

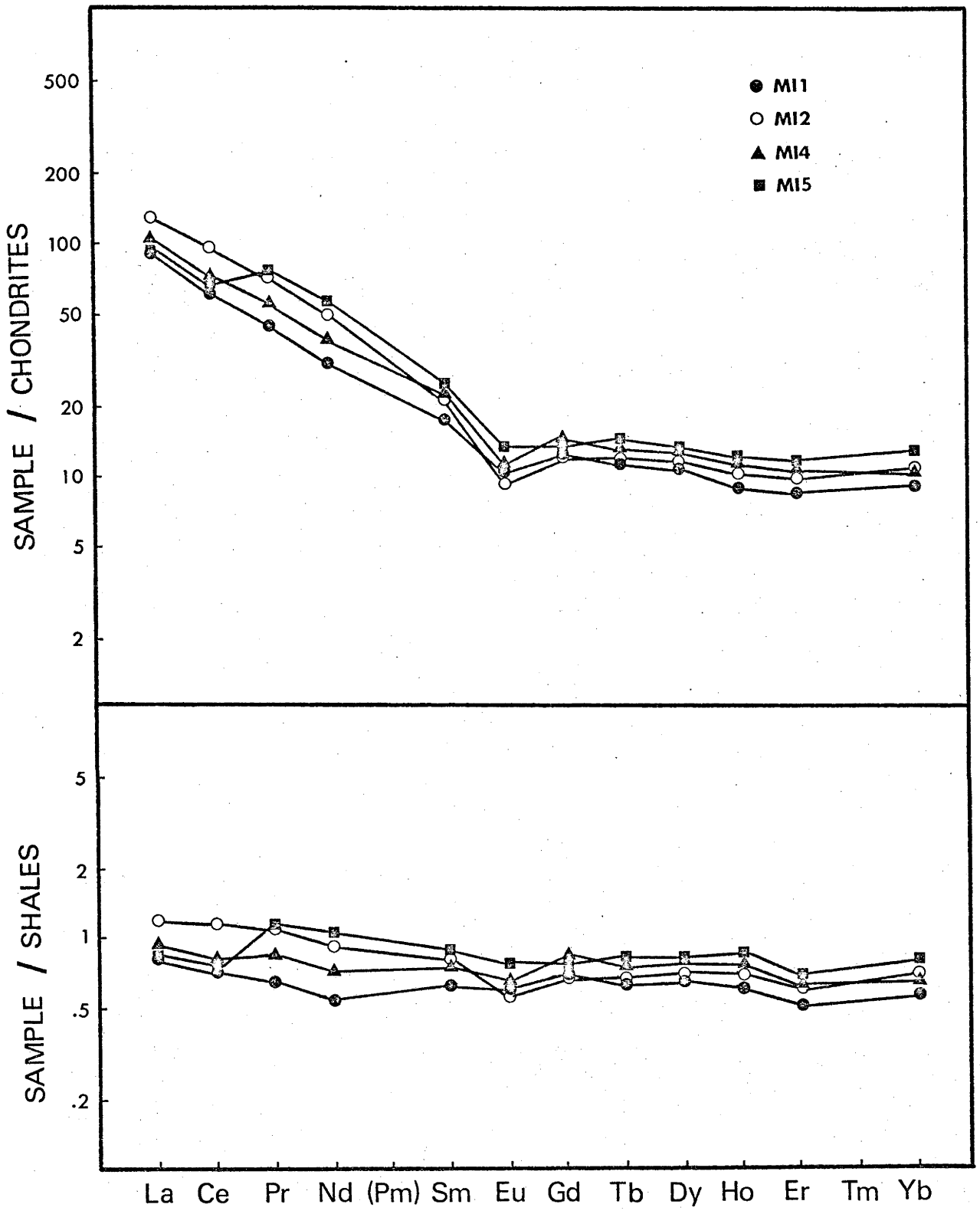

Fig. 4.4 Rare earth patterns for some Middle Proterozoic sediments from the Mt. Isa Group.

Amadeus Basin

Table 4.4 lists the trace element abundances of the Upper Proterozoic and Cambrian samples from the Amadeus Basin. Figs. 4.5, 4.6, and 4.7 show the chondrite and shale normalized rare earth patterns for these samples. Fig. 4.5 shows the rare earth patterns for the three Cambrian subgreywackes (A03, A04, A05) from the Arumbera sandstone. They show significant depletions in Eu relative to chondrites, but are nearly normal relative to the NASC. These samples show a large variation in ΣLREE/ΣHREE, which ranges from 6.5 to 13. ΣREE varies from 107 ppm to 137 ppm. Fig. 4.6 shows the rare earth patterns of three shales from the Upper Proterozoic Pertatatake Formation (A06, A07, A09). These three samples have similar rare earth patterns, and show a very small range in ΣREE (135 - 146 ppm). Another shale from the Pertatatake Formation (A010), shown in Fig. 4.7, is also very similar to these samples. All four samples have depletions of Eu relative to chondrites, but show no significant Eu anomalies relative to the NASC. They have nearly flat shale normalized rare earth patterns. The single sample from the Areyonga Formation, shown in Fig. 4.7, has a very similar rare earth pattern to the Pertatataka shales, but has a somewhat higher ΣREE of 186 ppm. The igneous rock (A014) from the Bitter Springs Formation is included in Table 4.4 and Fig. 4.7.

State Circle Shale

Trace element abundances in samples of the Silurian State Circle Shale are listed in Table 4.5. The chondrite and shale normalized rare earth patterns of these samples are shown in Figs. 4.8 and 4.9. All of these samples are depleted in Eu relative to chondrites, but they show no significant Eu anomaly relative to the NASC. The rare earth patterns of these samples are very similar, with the exception of SC2 which is somewhat lower in ΣREE (149 ppm) and ΣLREE/ΣHREE (7.2). The

Table 4.4 Rare earths and other trace elements in Upper Proterozoic sediments from the Amadeus Basin.

	A03	A04	A05	A06	A07	A09	A010	A012	A014
Th	10	9.4	7.8	16	14	10	15	17	1.2
U	1.7	1.5	1.4	2.9	2.7	2.1	2.6	2.5	0.25
Hf	6.4	7.4	4.2	4.2	4.7	4.0	4.3	3.9	2.4
Ba	220	300	440	280	210	240	240	440	160
Cs	7.1	4.7	3.0	12	21	15	17	28	1.1
La	24	29	22	28	29	29	34	41	7.8
Ce	52	64	56	62	65	61	63	86	21
Pr	6.3	6.7	4.3	6.5	7.6	6.3	7.0	8.9	2.6
Nd	19	21	14	22	23	22	24	27	11
Sm	4.3	3.1	2.8	4.5	4.6	3.9	5.3	5.4	3.0
Eu	0.87	0.61	0.55	0.85	0.91	0.71	1.0	1.0	1.0
Gd	4.7	3.2	2.6	3.6	3.9	3.5	4.8	4.1	3.8
Tb	0.76	0.53	0.33	0.65	0.69	0.55	0.71	0.75	0.59
Dy	4.1	3.2	1.8	3.7	4.2	3.3	3.7	4.2	3.5
Ho	1.0	0.75	0.41	0.79	0.94	0.76	0.87	1.1	0.81
Er	2.9	2.3	1.3	2.3	2.7	2.2	2.6	3.4	2.2
Yb	2.8	2.3	1.2	2.2	3.1	2.2	2.5	3.2	2.1
Σ REE	123	137	107	137	146	135	149	186	59
Y	28	24	9.0	17	17	17	20	23	20
Σ REE+Y	151	161	116	154	163	152	169	209	79
Eu/Eu^*	0.64	0.64	0.69	0.69	0.70	0.63	0.66	0.71	1.01
La/Yb	8.6	13	18	13	9.4	13	14	13	3.7
La/Sm	5.6	9.4	7.8	6.2	6.3	7.4	6.4	7.6	2.6
La/Th	2.4	3.1	2.8	1.8	2.1	2.9	2.3	2.4	6.5
Th/U	5.9	6.3	5.6	5.5	5.2	4.8	5.8	6.8	4.8
ΣLREE/ ΣHREE	6.5	10	13	9.3	8.2	9.8	8.9	10	3.4

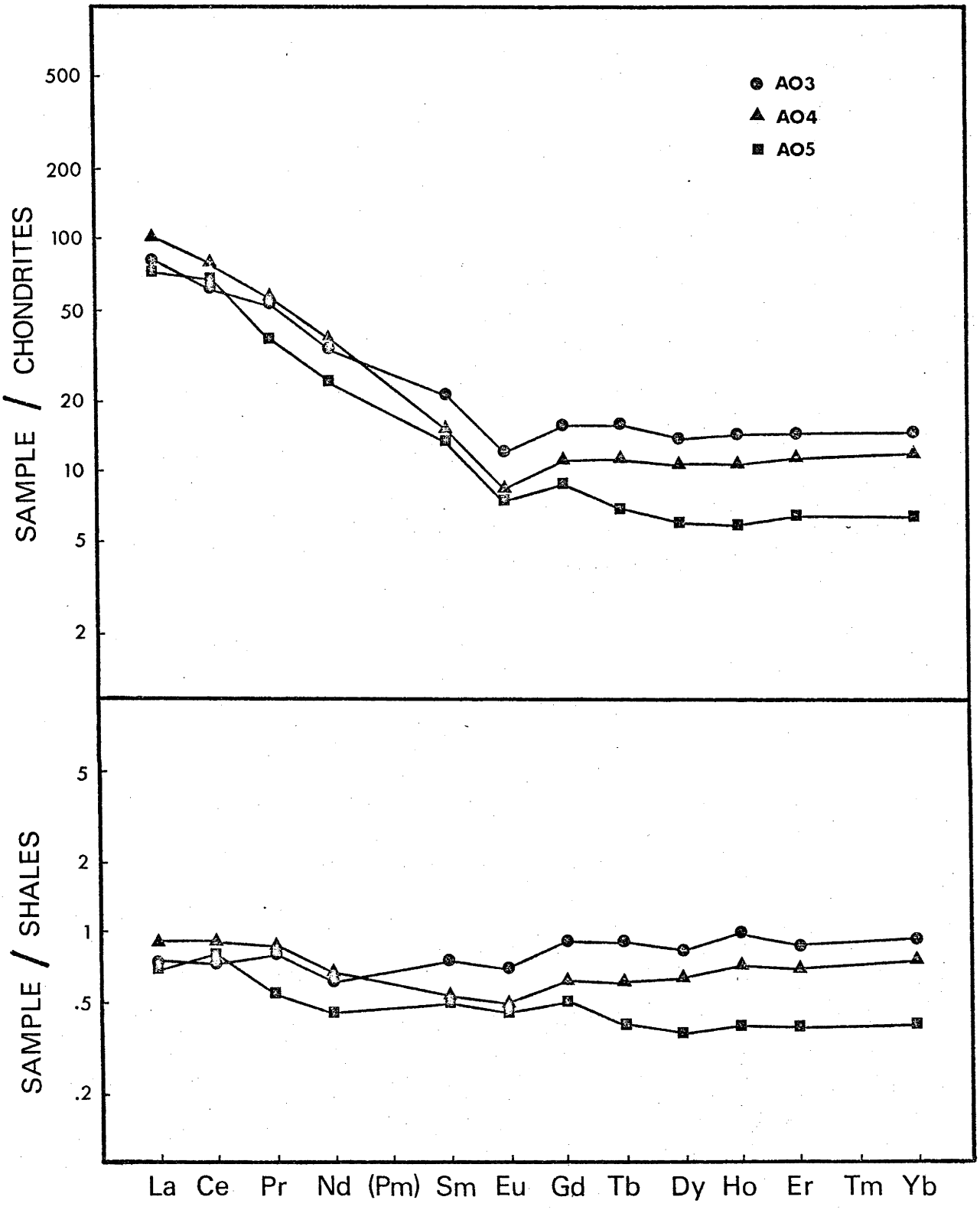

Fig. 4.5 Rare earth patterns for some Palaeozoic sediments from the Amadeus Basin.

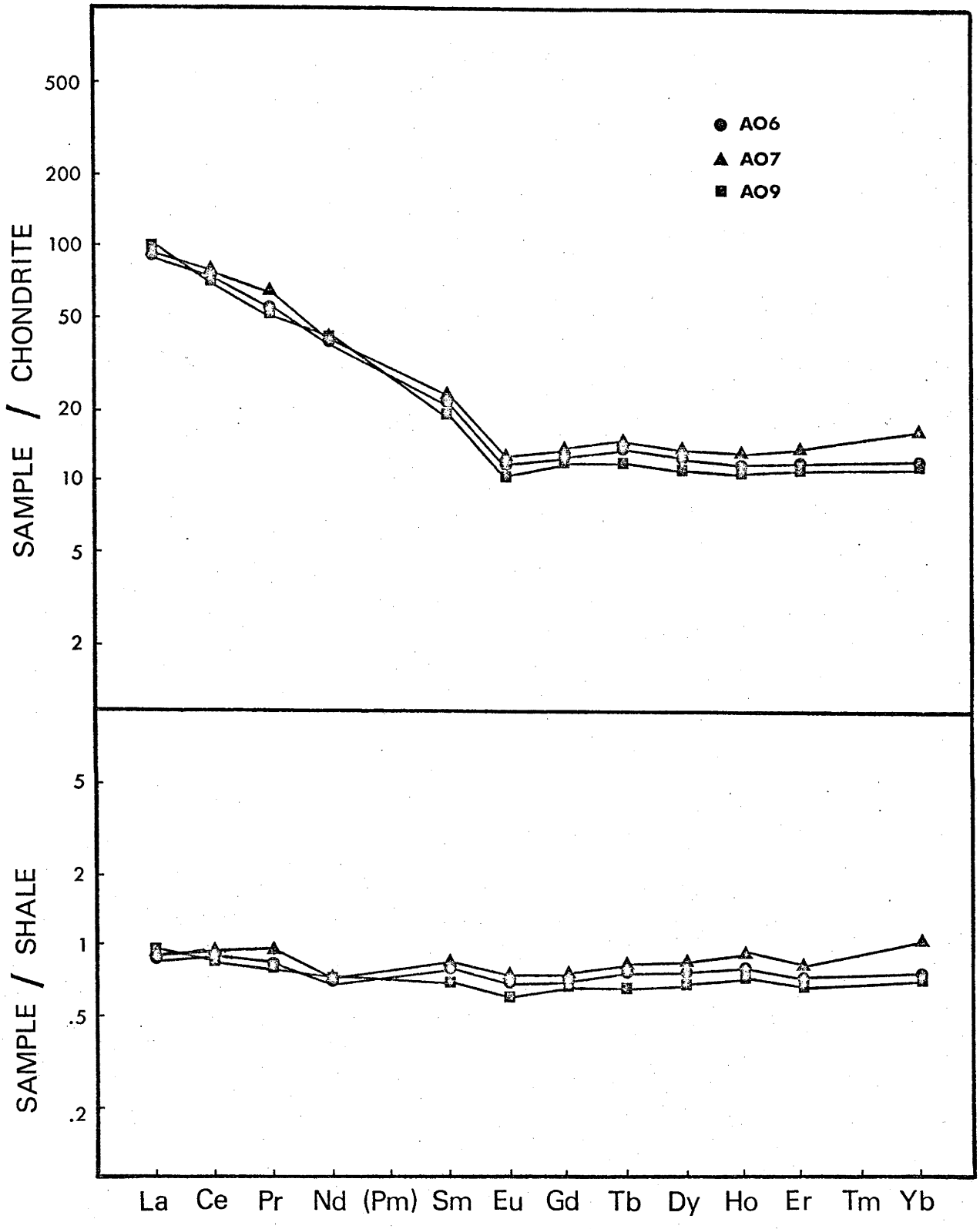

Fig. 4.6 Rare earth patterns for some Upper Proterozoic sediments from the Amadeus Basin.

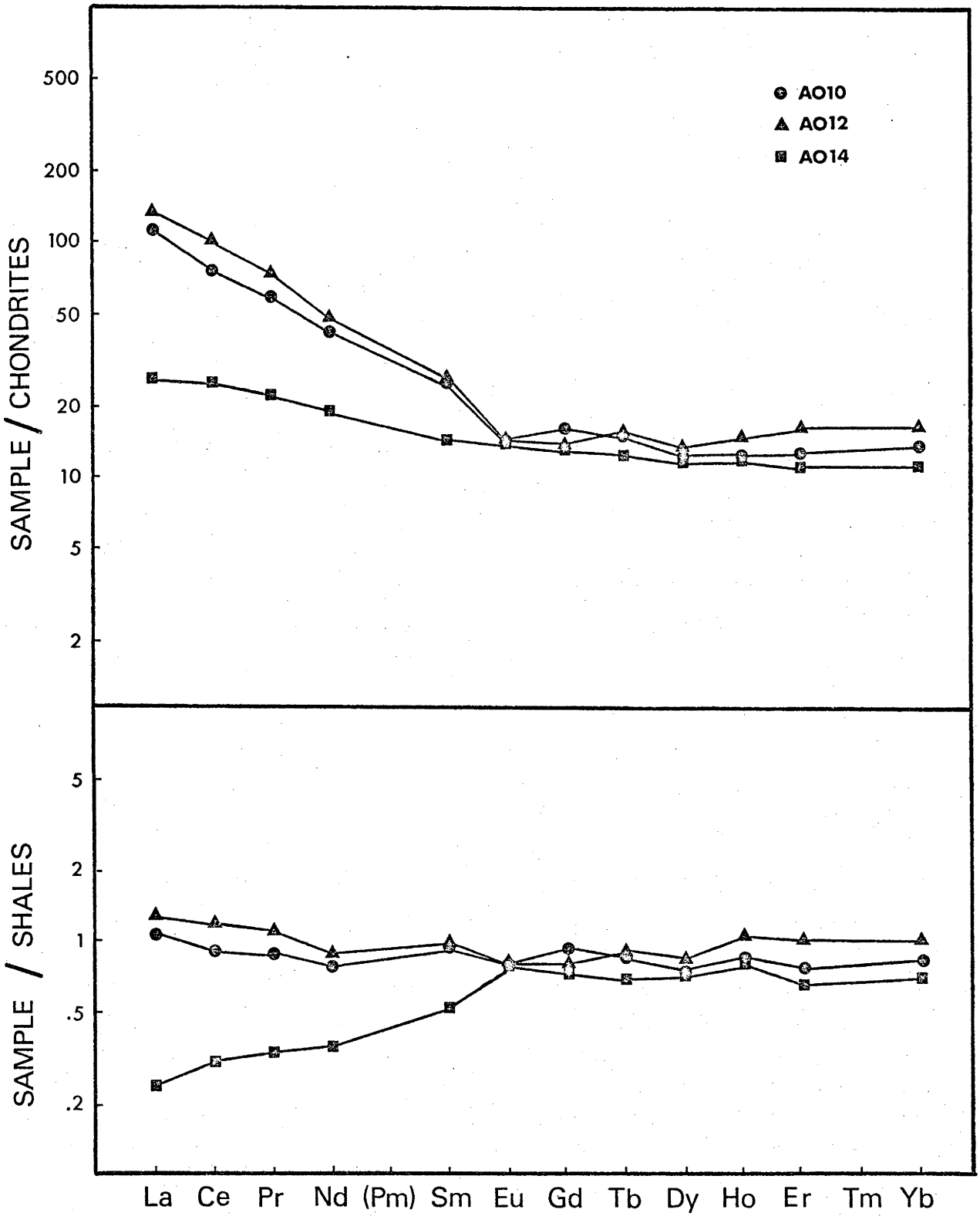

Fig. 4.7 Rare earth patterns for some Upper Proterozoic sediments from the Amadeus Basin. A014 is an igneous rock.

Table 4.5 Rare earths and other trace elements in Palaeozoic sediments from the State Circle Shale.

	SC1	SC2	SC3	SC4	SC5	SC7	SC8
Th	15	13	14	14	13	15	16
U	3.1	2.7	2.3	2.8	2.5	2.3	2.7
Hf	4.0	3.1	3.2	3.3	2.5	2.3	3.0
Ba	520	330	450	500	400	390	470
Cs	15	10	11	13	11	11	13
La	46	32	37	44	41	40	44
Ce	98	59	74	95	83	85	94
Pr	10	8.1	8.0	9.7	8.4	11	8.1
Nd	31	25	26	29	26	32	29
Sm	6.4	5.6	5.8	6.2	5.4	5.3	5.0
Eu	1.3	1.2	1.1	1.3	1.1	0.99	0.95
Gd	4.8	6.1	4.7	5.2	4.5	4.3	4.7
Tb	0.82	0.84	0.75	0.86	0.71	0.68	0.74
Dy	4.5	4.6	3.8	5.0	4.4	3.9	4.0
Ho	1.0	0.99	0.94	1.1	0.91	0.83	0.89
Er	3.1	2.6	2.8	3.0	2.8	2.3	2.5
Yb	2.9	2.6	2.7	2.9	2.7	2.3	2.4
Σ REE	210	149	168	203	181	188	196
Y	28	19	27	25	21	24	34
Σ REE+Y	238	168	195	228	202	212	230
Eu/Eu^*	0.77	0.66	0.66	0.73	0.71	0.67	0.64
La/Yb	16	12	14	15	15	17	18
La/Sm	7.2	5.7	6.4	7.1	7.6	7.5	8.8
La/Th	3.1	2.5	2.6	3.1	3.2	2.7	2.8
Th/U	4.8	4.8	6.1	5.0	5.2	6.5	5.9
ΣLREE/ ΣHREE	11	7.1	9.6	10	10	12	12

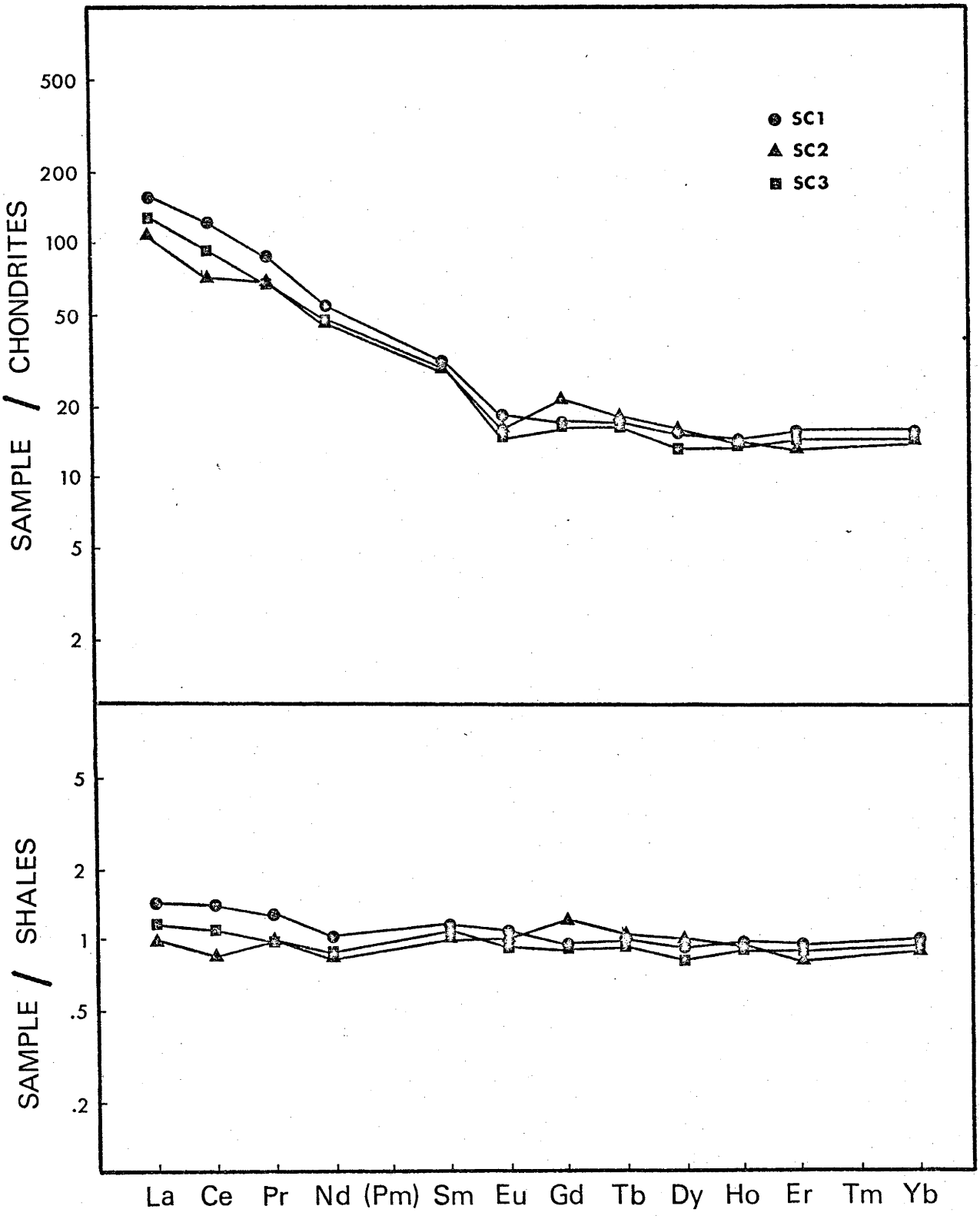

Fig. 4.8 Rare earth patterns for some Palaeozoic sediments from the State Circle Shale.

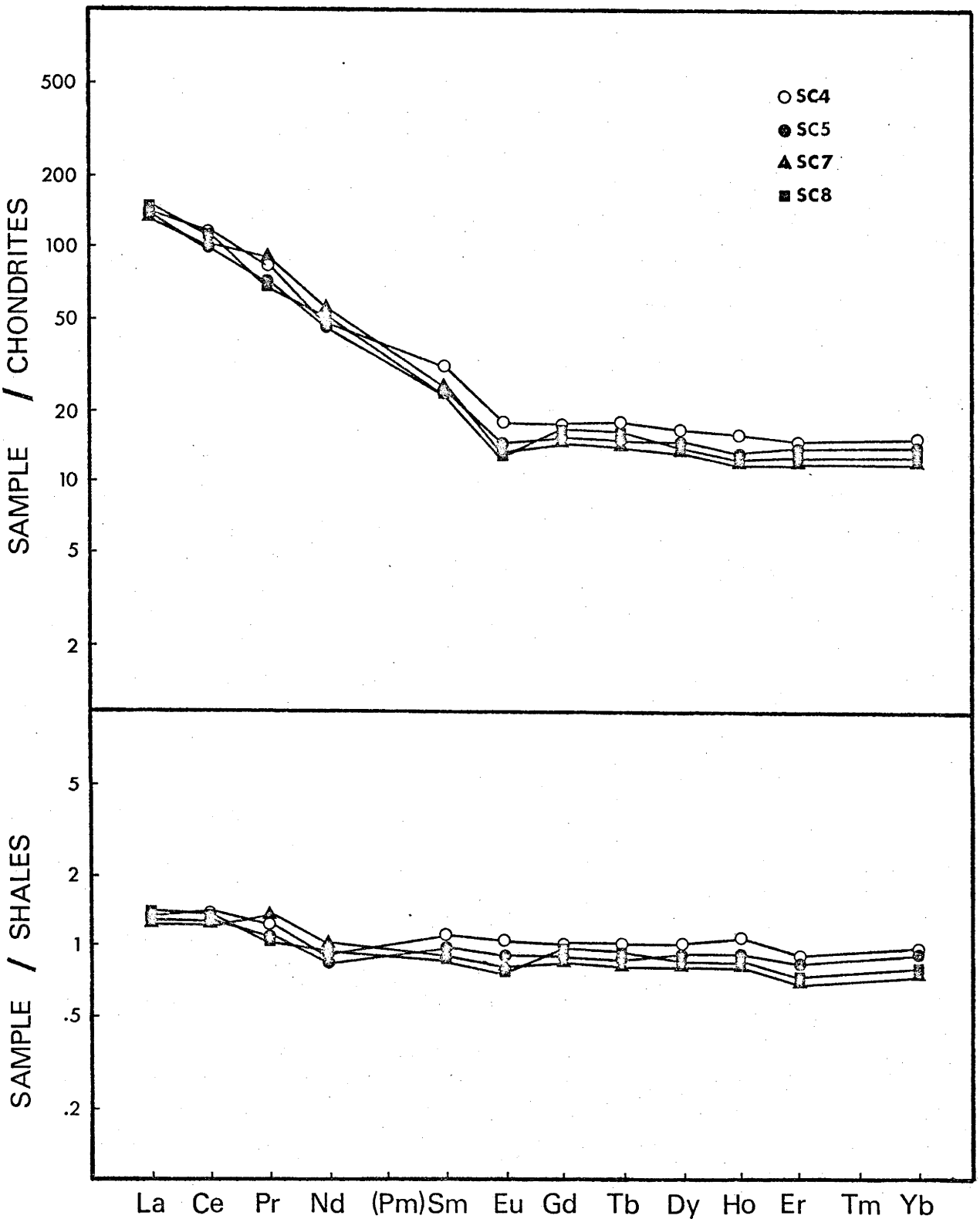

Fig. 4.9 Rare earth patterns for some Palaeozoic sediments from the State Circle Shale.

remaining six samples range in ΣREE from 168 - 210 ppm, and in ΣLREE/ΣHREE from 9.6 - 12.

Baldwin Formation

Trace element abundances in the Devonian greywackes from the Baldwin Formation are listed in Table 4.6. Figs. 4.10 and 4.11 show the chondrite and shale normalized rare earth patterns of these samples. Two of the samples (M284, M285) show a significant enrichment of Eu relative to chondrites, and the remaining samples show no significant enrichment or depletion of Eu relative to chondrites. All of these samples are enriched in Eu relative to the NASC. ΣLREE/ΣHREE ratios are low and range from 5.6 to 2.7. All of the samples show a strong depletion in the lightest rare earths relative to the NASC. ΣREE are also low and range from 45 - 66 ppm.

Canning Basin

Table 4.7 lists the trace element abundances of the Palaeozoic samples from the Canning Basin. Figs. 4.12 and 4.13 show the chondrite and shale normalized rare earth patterns of these samples. The three Permian orthoquartzites (PL3, PL4, PL5) from the Grant Formation, and the Carboniferous arenaceous limestone (PL8) from the Laurel Formation are shown in Fig. 4.12. All four samples have low ΣREE in the range 23 - 30 ppm. ΣLREE/ΣHREE of these samples is in the range 6.2 - 8.1. The samples are depleted in Eu relative to chondrites, but show no significant Eu anomalies relative to the NASC. Rare earth patterns of the Permian shale from the Poole Sandstone (PL1), and the Carboniferous shale (PL6) and siltstone (PL7) from the Laurel Formation are shown in Fig. 4.13. These samples are depleted in Eu relative to chondrites, but are not depleted or enriched relative to the NASC. ΣLREE/ΣHREE for the two shales are 9.1 and 13, and for the siltstone it is 8.0. PL6 is somewhat enriched in the light rare earths relative to the NASC, but

Table 4.6 Rare earths and other trace elements in Palaeozoic sediments from the Baldwin Formation

	M216	M277	M282	M283	M284	M285	B10
Th	2.1	0.88	1.3	0.72	0.72	1.4	1.1
U	0.59	0.32	0.44	0.28	0.26	0.84	0.40
Hf	2.2	1.8	2.5	1.6	1.3	1.2	2.0
Ba	330	85	130	42	130	100	170
Cs	1.1	0.41	0.18	0.16	0.50	0.80	0.50
La	11	10	8.0	6.3	5.4	6.8	7.2
Ce	26	18	19	16	15	15	18
Pr	3.5	2.2	3.2	2.0	1.9	2.0	2.5
Nd	12	10	13	8.6	8.5	8.2	11
Sm	2.9	2.8	3.6	2.5	2.7	2.2	3.1
Eu	0.89	0.97	1.2	0.85	1.4	1.1	1.0
Gd	3.2	3.4	4.3	3.0	3.3	2.6	3.5
Tb	0.43	0.52	0.62	0.47	0.48	0.39	0.52
Dy	2.6	3.1	3.9	3.0	3.1	2.7	3.3
Ho	0.53	0.79	0.95	0.70	0.79	0.59	0.81
Er	1.5	2.2	2.8	2.0	2.3	1.9	2.4
Yb	1.4	2.3	2.8	2.2	2.3	1.8	2.3
Σ REE	66	56	63	48	47	45	56
Y	17	19	21	24	22	15	23
Σ REE+Y	83	75	84	72	69	60	79
Eu/Eu^*	0.98	1.06	1.00	1.05	1.53	1.55	1.04
La/Yb	7.9	4.3	2.9	2.9	2.3	3.8	3.1
La/Sm	3.8	3.6	2.2	2.5	2.0	3.1	2.3
La/Th	5.2	11	6.2	8.8	7.5	4.9	6.5
Th/U	3.6	2.8	3.0	2.6	2.8	1.7	2.8
ΣLREE/ ΣHREE	5.6	3.5	3.2	3.2	2.7	3.5	3.2

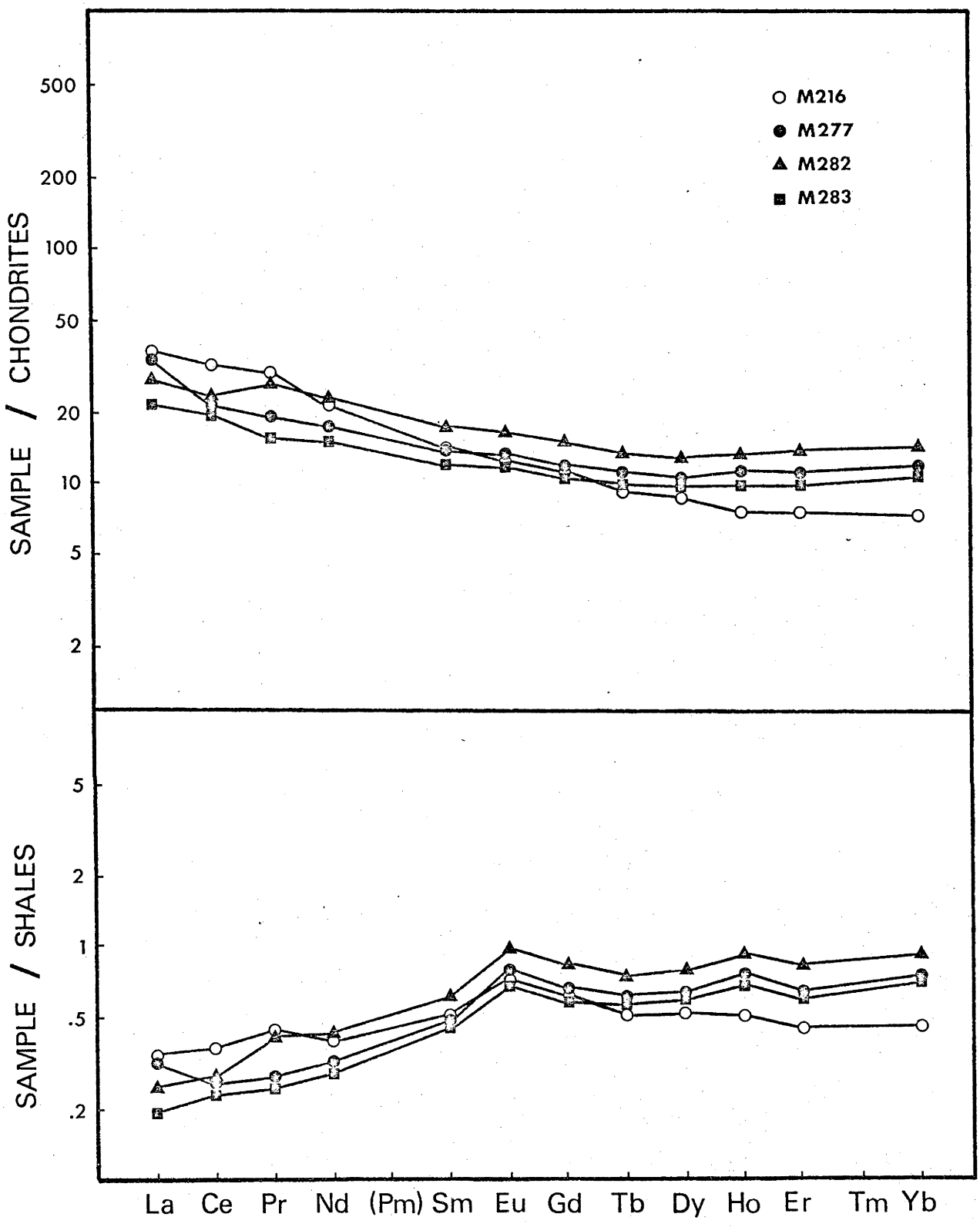

Fig. 4.10 Rare earth patterns for some Palaeozoic sediments from the Baldwin Formation.

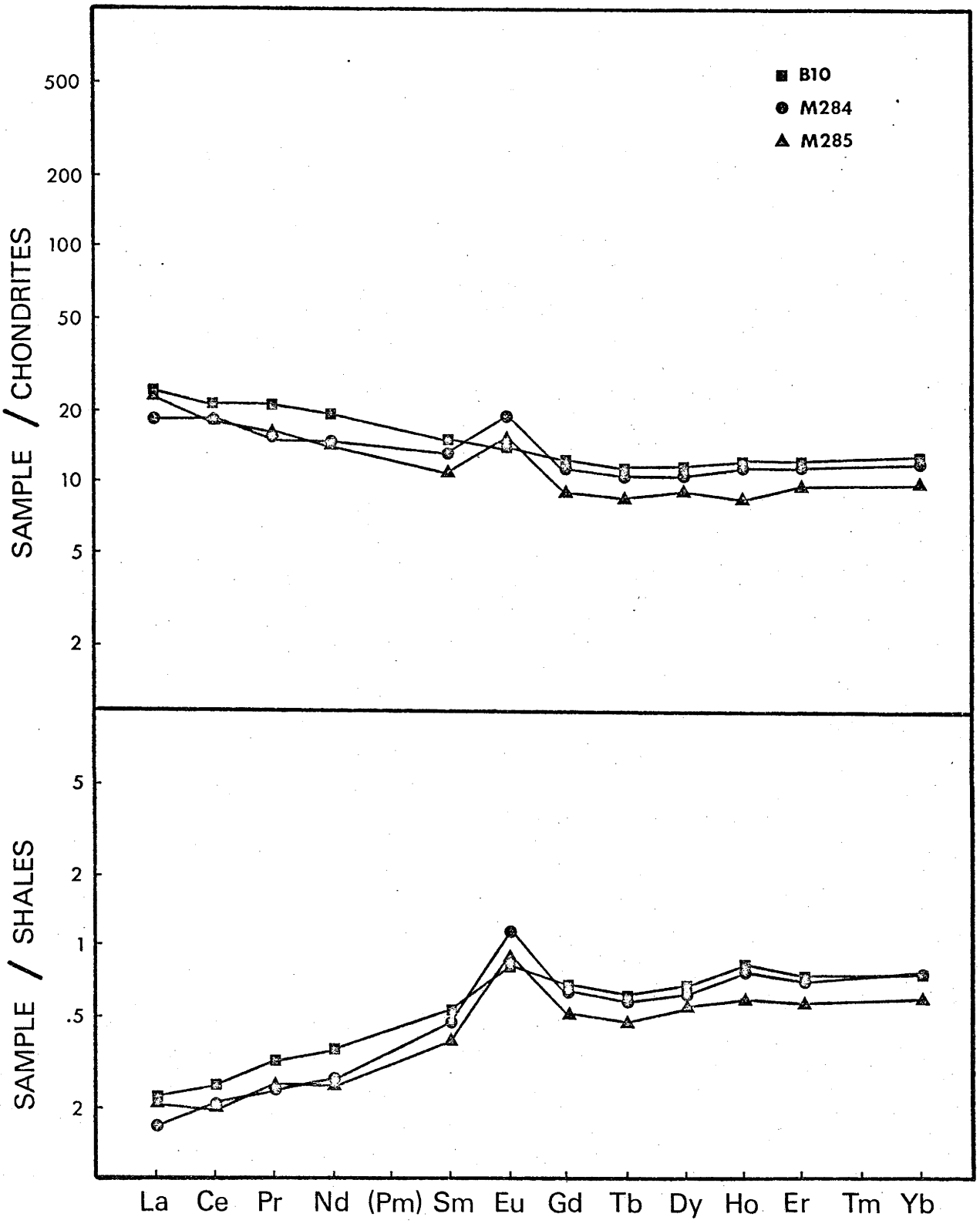

Fig. 4.11 Rare earth patterns for some Palaeozoic sediments from the Baldwin Formation.

Table 4.7 Rare earths and other trace elements in Palaeozoic sediments from the Canning Basin.

	PL1	PL3	PL4	PL5	PL6	PL7	PL8
Th	18	2.1	1.8	2.3	15	5.0	1.8
U	2.9	0.53	0.54	0.50	2.5	4.3	0.96
Hf	4.9	2.8	1.6	2.8	3.1	5.4	1.9
Ba	590	240	110	81	500	290	33
Cs	17	0.57	0.41	0.29	18	12	0.42
La	40	6.6	4.7	5.8	52	35	5.3
Ce	86	13	9.7	12	132	72	8.9
Pr	9.1	1.3	1.1	1.2	12	8.4	1.1
Nd	30	4.2	3.6	3.9	37	25	3.5
Sm	6.0	0.79	0.70	0.80	6.5	5.7	0.79
Eu	1.1	0.21	0.18	0.16	1.2	1.1	0.17
Gd	4.7	0.98	0.93	0.97	5.2	4.9	0.84
Tb	0.82	0.15	0.12	0.12	0.84	0.84	0.13
Dy	5.0	1.0	0.80	0.76	4.6	5.0	0.83
Ho	1.2	0.18	0.16	0.14	1.1	1.1	0.20
Er	3.6	0.55	0.50	0.40	3.2	3.1	0.56
Yb	3.6	0.64	0.56	0.50	2.8	3.5	0.59
Σ REE	192	30	23	26	258	166	23
Y	29	5.0	3.5	5.2	36	31	4.2
Σ REE+y	221	35	27	31	294	197	27
Eu/Eu^*	0.66	0.79	0.75	0.63	0.67	0.66	0.71
La/Yb	11	10	8.4	12	19	10	9.0
La/Sm	6.7	8.3	6.7	7.2	8.0	6.1	6.7
La/Th	2.2	3.1	2.6	2.5	3.5	7.0	2.9
Th/U	6.2	4.0	3.3	4.6	6.0	1.2	1.9
ΣLREE/ ΣHREE	9.1	7.5	6.6	8.1	13	8.0	6.2

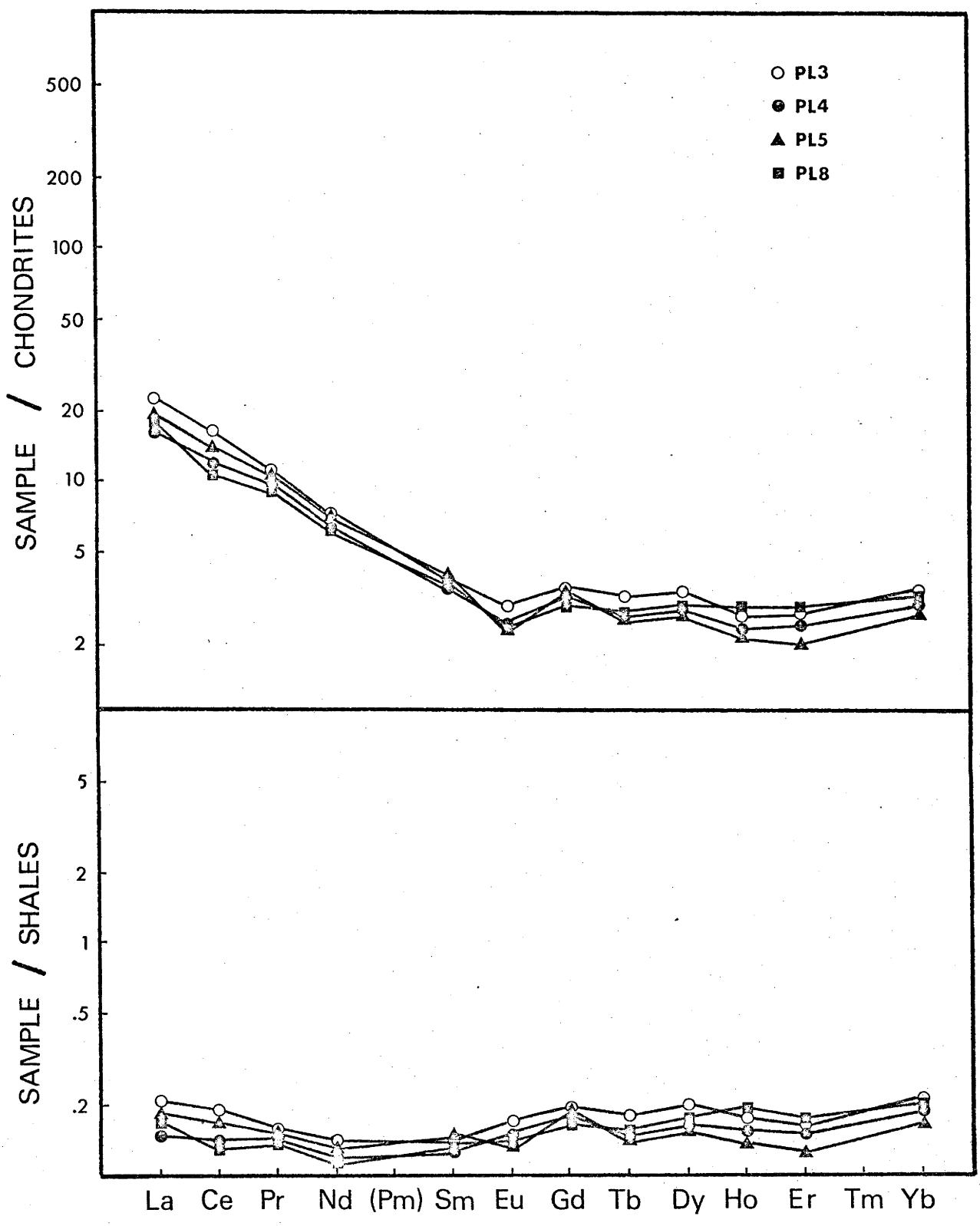

Fig. 4.12 Rare earth patterns for some Palaeozoic sediments from the Canning Basin.

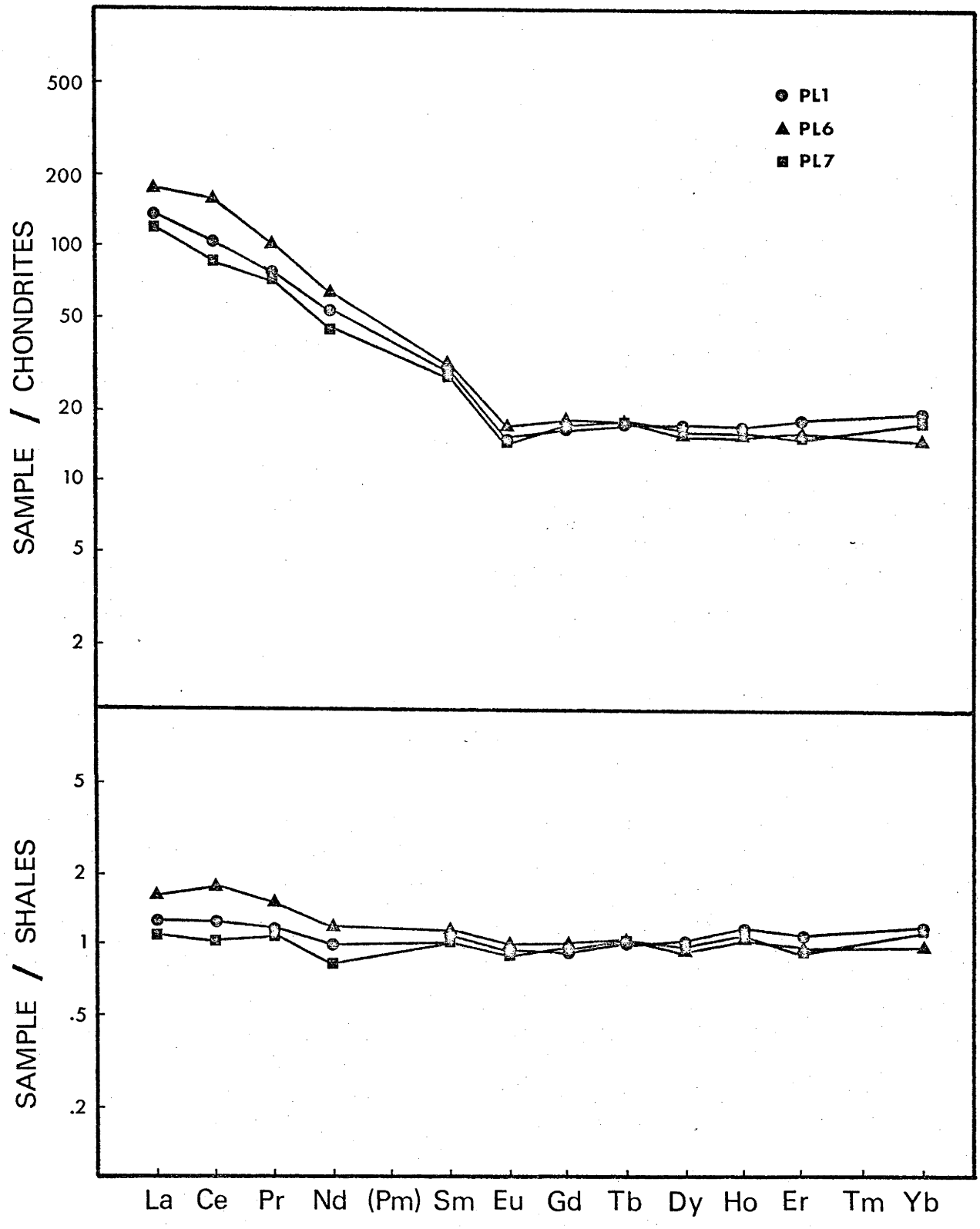

Fig. 4.13 Rare earth patterns for some Palaeozoic sediments from the Canning Basin.

PL1 and PL7 have nearly flat shale normalized rare earth patterns.

Perth Basin

The trace element abundances in the Palaeozoic and Mesozoic samples from the Perth Basin are listed in Table 4.8. Fig. 4.14 shows the chondrite and shale normalized rare earth patterns of three Triassic shales (PW4, PW5, PW7) from the Kockatea Shale, and a Permian subgreywacke (PW8) from the Caryngina Formation. All four samples are depleted in Eu relative to chondrites, but show no significant Eu anomalies relative to the NASC. ΣLREE/ΣHREE for PW7 is 7.0, and for the other three samples it ranges from 9.4 - 11. PW7 is slightly depleted in the light rare earths in the shale normalized pattern, and PW8 is slightly enriched in the light rare earths. The shale normalized rare earth patterns of PW4 and PW5 are nearly flat. Fig. 4.15 shows the rare earth patterns of a Triassic arkose from the Woodada Formation (PW2), and two Permian subgreywackes (PW9, PW10) from the Caryngina Formation. The arkose has low ΣREE (92 ppm), but its rare earth pattern is similar to that of the NASC in most other respects. The two subgreywackes (PW9, PW10) also have nearly flat shale normalized rare earth patterns. ΣREE of PW9 and PW10 is 133 and 200 ppm. All three samples shown in Fig. 4.15 show depletions in Eu relative to chondrites, but show no significant Eu anomaly relative to the NASC.

Carnarvon Basin

The trace element abundances of the Cenozoic and Mesozoic sediments from the Carnarvon Basin are listed in Table 4.9. Fig. 4.16 shows the chondrite and shale normalized rare earth patterns of these samples. The Eocene calcarenaceous sandstone (CL1) from the Giralia Calcarenite has low ΣREE (53 ppm), and is depleted in the light rare earths in the shale normalized rare earth pattern. One Jurassic mudstone (CL2) from the Wogatti Formation has higher ΣREE (179 ppm), and is

Table 4.8 Rare earths and other trace elements in Palaeozoic and Mesozoic sediments from the Perth Basin.

	PW2	PW4	PW5	PW7	PW8	PW9	PW10
Th	5.9	22	19	12	14	14	19
U	1.3	4.5	3.3	3.4	2.3	2.6	3.7
Hf	4.7	5.2	4.3	5.3	3.5	14	17
Ba	310	620	580	470	450	250	390
Cs	0.93	12	10	6.8	7.9	3.5	7.9
La	18	56	50	40	35	29	42
Ce	42	115	104	82	79	55	91
Pr	4.8	14	13	8.9	7.5	6.5	8.4
Nd	15	43	43	30	24	22	31
Sm	2.8	8.7	8.2	6.3	4.8	4.8	6.0
Eu	0.61	1.8	1.7	1.4	0.92	0.80	1.0
Gd	3.0	7.2	6.7	6.1	4.2	3.9	5.1
Tb	0.40	1.1	1.2	1.1	0.71	0.61	0.85
Dy	2.6	6.4	6.2	6.1	4.0	3.7	5.0
Ho	0.51	1.6	1.4	1.4	0.86	0.84	1.2
Er	1.6	4.5	3.8	4.3	2.3	2.7	3.6
Yb	1.6	4.3	3.7	4.7	2.1	2.8	3.7
Σ REE	92	263	242	193	167	133	200
Y	13	33	38	32	28	17	41
Σ REE+Y	105	296	280	225	195	150	241
Eu/Eu^*	0.71	0.72	0.74	0.78	0.67	0.60	0.61
La/Yb	11	13	14	8.5	17	10	11
La/Sm	6.4	6.4	6.1	6.3	7.3	6.0	7.0
La/Th	3.1	2.5	2.6	3.3	2.5	2.1	2.2
Th/U	4.5	4.9	5.9	3.5	6.1	5.4	5.1
ΣLREE/ ΣHREE	8.5	9.4	9.4	7.0	11	7.7	9.2

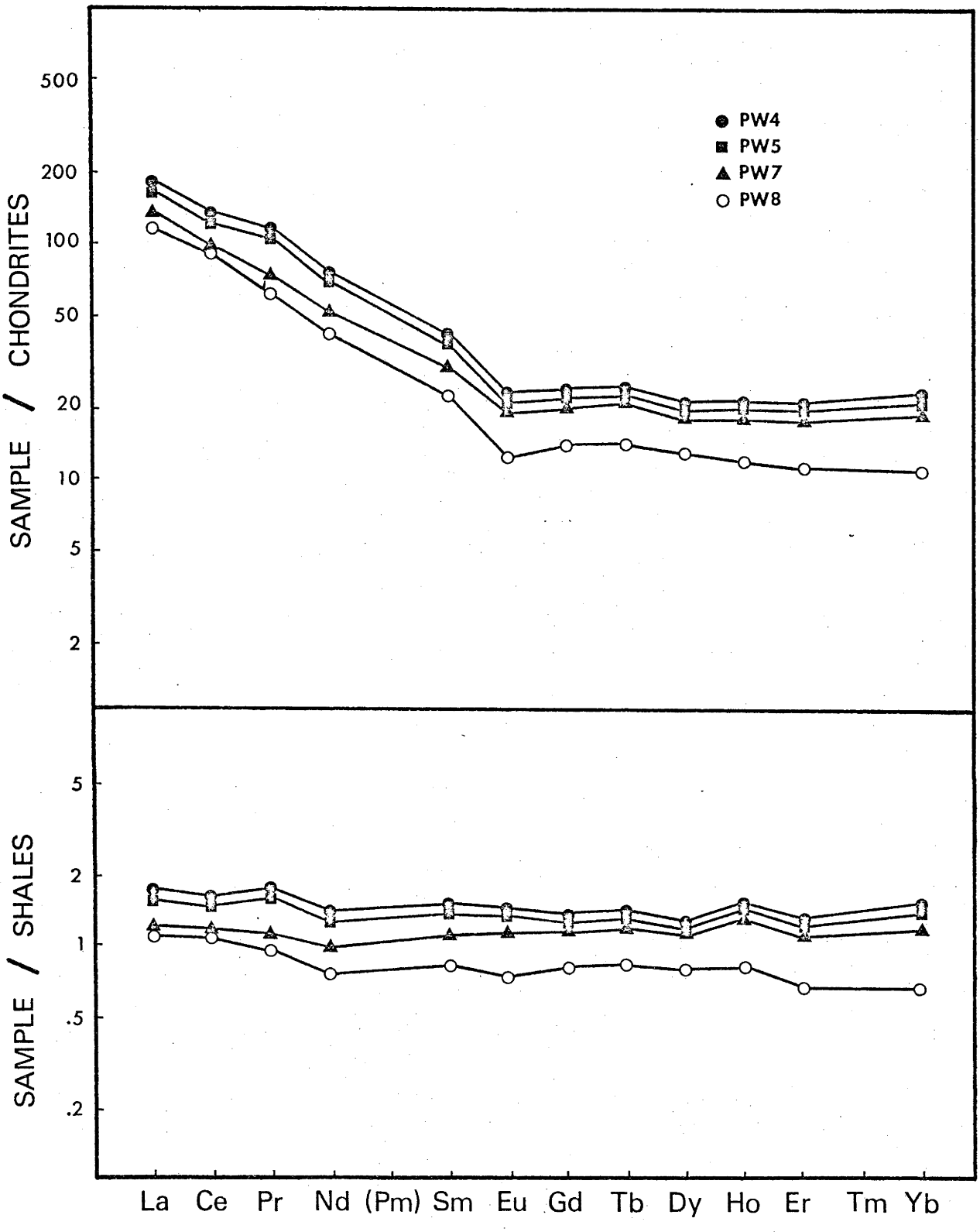

Fig. 4.14 Rare earth patterns for some Mesozoic and Palaeozoic sediments from the Perth Basin.

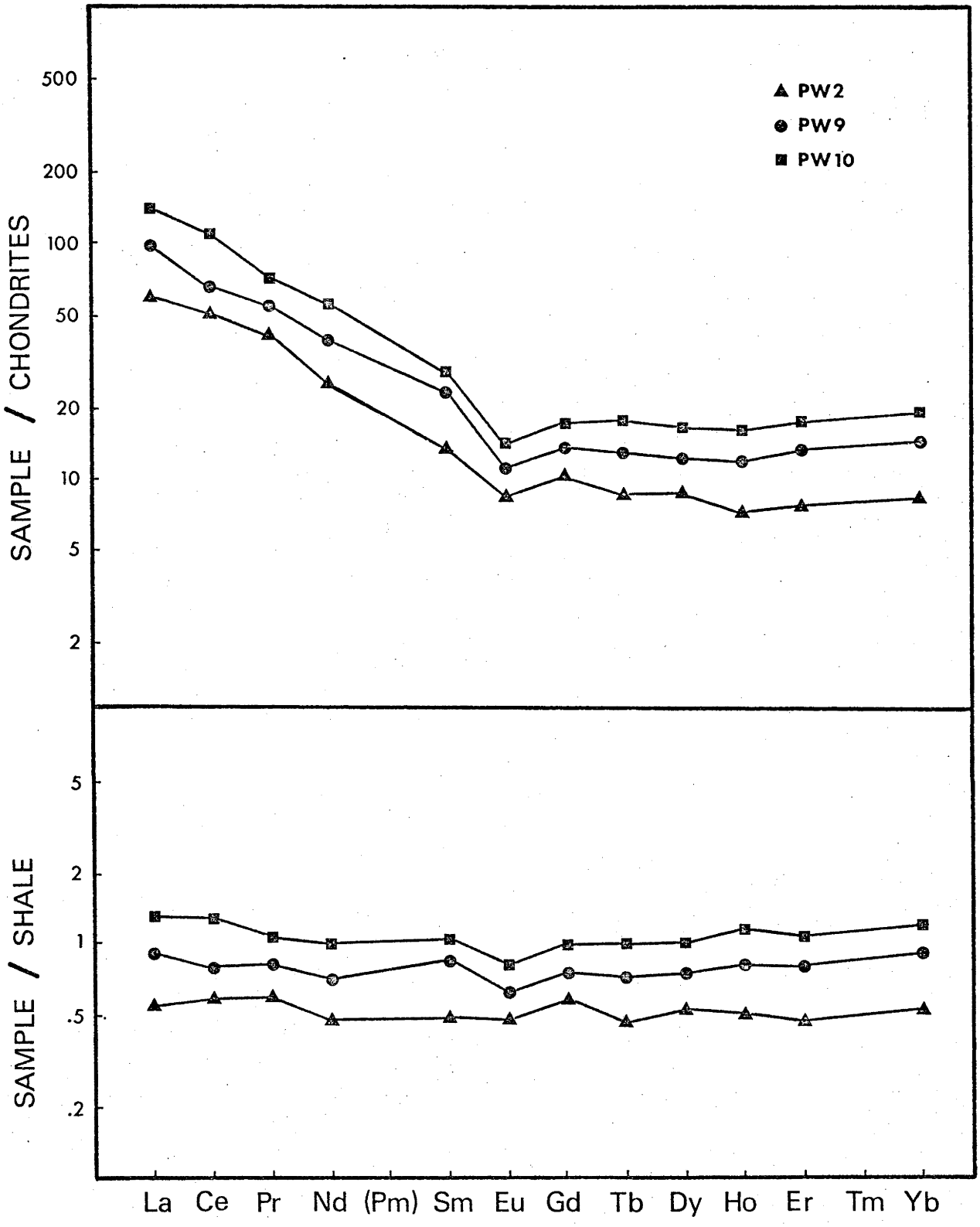

Fig. 4.15 Rare earth patterns for some Mesozoic and Palaeozoic sediments from the Perth Basin.

Table 4.9 Rare earths and other trace elements in Mesozoic and Cenozoic sediments from the Carnarvon Basin.

	CL1	CL2	CL3	CL4
Th	6.0	7.5	26	21
U	1.6	3.3	3.7	2.6
Hf	5.9	6.0	8.2	3.8
Ba	81	110	70	42
Cs	1.3	5.7	6.8	14
La	9.7	32	16	7.0
Ce	24	87	33	19
Pr	2.6	8.9	3.4	1.6
Nd	8.3	32	11	6.1
Sm	1.7	5.6	2.5	1.6
Eu	0.26	1.0	0.53	0.36
Gd	1.4	4.0	3.1	2.1
Tb	0.25	0.61	0.61	0.38
Dy	1.5	3.6	4.2	2.9
Ho	0.41	0.84	1.1	0.69
Er	1.2	2.1	3.2	2.1
Yb	1.4	2.1	3.3	2.1
Σ REE	53	179	81	46
Y	11	20	35	18
Σ REE+Y	64	199	116	64
Eu/Eu*	0.56	0.70	0.64	0.66
La/Yb	6.9	15	4.8	3.3
La/Sm	5.7	5.7	6.4	4.3
La/Th	1.6	4.3	0.62	0.33
Th/U	3.8	2.3	7.0	8.1
ΣLREE/ ΣHREE	7.7	12.4	4.2	3.4

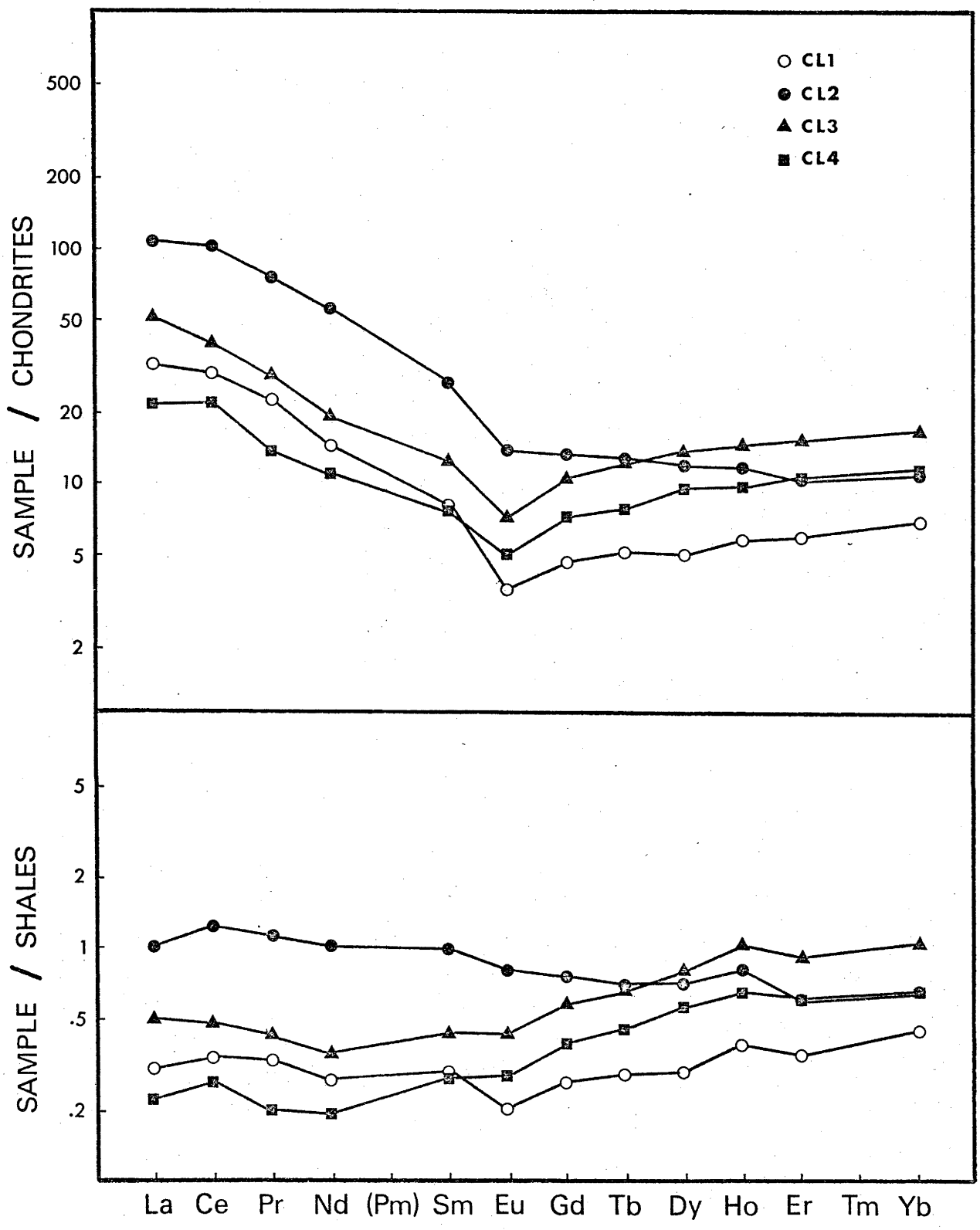

Fig. 4.16 Rare earth patterns for some Cenozoic and Mesozoic sediments from the Carnarvon Basin.

enriched in the light rare earths in the shale normalized pattern. Two other Jurassic mudstones from the Wogatti Sandstone (CL3, CL4) have low ΣREE (81 and 46 ppm), and have light rare earth depleted shale normalized patterns. All of the samples from the Carnarvon Basin are depleted in Eu relative to chondrites, but are nearly normal in Eu relative to the NASC.

Chapter 5

Discussion

Variations in rare earth patterns

Introduction

Ronov et al. (1967) and Ronov et al. (1972) have shown that the distribution of the rare earths in sediments is controlled both by the composition of the source rocks and the enrivonment of weathering and deposition. The small range of variation usually observed in sedimentary rare earth patterns is due to the "averaging" effect of mixing of upper crustal material in the sedimentary cycle. The mixing effect is strongest during deposition in the marine basins, which usually receive material from a wide area of continental crust. It is weakest for sediments deposited in a continental environment, where transportation and deposition is slow and weathering prolonged. The sediments analyzed in my study were mainly deposited in marine basins, and so it is possible that they represent the average upper crustal material at the time of deposition. In the discussion which follows, consideration will be restricted to the shales, siltstones, greywackes, and subgreywackes, since they seem more likely to retain the rare earth distribution of their source rocks. This will exclude samples CL1, PL3, PL4, PL5, PL8 and PW2. In the following discussion, I will attempt to determine the extent to which variations in rare earth distributions occur among the samples, and then consider the possible causes.

Eu anomalies

It is clear from the results presented in chapter four that the samples can be divided into two groups on the basis of relative Eu distribution. The Archaean sediments from the Eastern Goldfields

Province and the Devonian greywackes from the Baldwin Formation are characterized by the absence of significant negative Eu anomalies relative to chondrites. All other samples have negative Eu anomalies of about the same order as the NASC. The average Eu/Eu^* for the Archaean samples is 1.23 ± 0.20 (average ± standard deviation), and for the Devonian greywackes it is 1.17 ± 0.25. The remaining samples (hereafter called the Eu depleted samples) have an average Eu/Eu^* of 0.67 ± 0.05. The negative Eu anomaly of the Eu depleted samples is remarkably constant. It shows no sign of changing through time. The average Eu/Eu^* for the Middle Proterozoic samples is 0.65, and so it is not distinguishable from that of the younger samples. Wildeman and Haskin (1973) noted that their data was consistent with a gradual depletion in Eu in sediments from chondritic values in the Archaean down to that of the NASC at about 500 million years ago. That interpretation is clearly not consistent with the results presented here.

ΣLREE/ΣHREE ratios

The average ΣLREE/ΣHREE for the 31 Eu depleted samples is 9.4 ± 2.3. Only two samples fall outside a range of two standard deviations from the average. These are two samples (CL3, CL4) from the Carnarvon Basin, which have ΣLREE/ΣHREE of 4.2 and 3.4 If these two samples are excluded from the group, then the average ΣLREE/ΣHREE for the Eu depleted samples is 9.8 ± 1.8. The consistent nature of rare earth patterns in the Eu depleted samples is best shown by the fact that variations between samples from different localities are not larger than the variations among samples from the same locality. The average ΣLREE/ΣHREE for samples from the Mt. Isa Group, the Amadeus Basin, the State Circle Shale, the Canning Basin, and the Perth Basin are 10.1 ± 1.9, 9.5 ± 1.8, 10.2 ± 1.7, 10.0 ± 2.6 and 9.0 ± 1.4. When the average ΣLREE/ΣHREE for each of these five groups are averaged the result is 9.8 ± 0.5, which compares with 9.8 ± 1.8

when the samples are averaged individually. Thus, with the exception of two samples, these samples form a consistent group with respect to ΣLREE/ΣHREE ratios.

The consistent nature of ΣLREE/ΣHREE ratios among the Eu depleted samples is in sharp contrast to those of the Archaean sediments and the Devonian greywackes from the Baldwin Formation. One Archaean sample (KH41) is highly depleted in ΣREE and has a value of 3.5 for ΣLREE/ΣHREE. The remaining nine Archaean samples can be divided into two groups on the basis of ΣLREE/ΣHREE ratios. One group (KH21, KH30, KH32) is depleted in the heaviest rare earths relative to the NASC, and the other group (KH1, KH36, KH38, KH44, KH37, KH47) are slightly depleted in the light rare earths relative to the NASC. The average ΣLREE/ΣHREE for the group depleted in the heaviest rare earths is 15 $\pm$ 4. The average ΣLREE/ΣHREE for the group depleted in the light rare earths is 6.3 $\pm$ 0.5. The average ΣLREE/ΣHREE of the group depleted in the heavy rare earths is higher than any of those of the Eu depleted samples. The average ΣLREE/ΣHREE of the group depleted in the light rare earths is lower than any of those of the Eu depleted samples (excluding CL3 and CL4). The average ΣLREE/ΣHREE of the Devonian volcanic greywackes is 3.6 $\pm$ 0.9. Thus, both the Archaean sediments and the Devonian greywackes are distinctly different to the Eu depleted sediments with respect to ΣLREE/ΣHREE ratios as well as Eu distribution.

Absolute abundances

The average ΣREE for the Archaean samples (excluding KH41) is 91 $\pm$ 34 ppm, and for the Devonian greywackes it is 54 $\pm$ 8 ppm. The average ΣREE for the Eu depleted group is 171 $\pm$ 41 ppm. The average ΣREE for the samples from the Mt. Isa Group, the Amadeus Basin, the State Circle Shale, the Canning Basin, and the Perth Basin are 143 $\pm$ 23, 140 $\pm$ 20, 185 $\pm$ 21, 205 $\pm$ 47, and 200 $\pm$ 48 respectively. It can be seen from

this that the samples from the Middle Proterozoic Mt. Isa Group and the Upper Proterozoic and Cambrian samples of the Amadeus Basin are somewhat lower in ΣREE than the younger samples. The ΣREE of the Archaean samples and the Devonian greywackes are distinctly lower than those of the Eu depleted group of samples.

Summary

The samples analyzed in this study fall into two distinct groups, one which is deficient in Eu relative to chondrites and one which is not. The samples which are deficient in Eu show very little variation in their relative rare earth patterns, but they seem to show a trend of increasing ΣREE with decreasing age. The samples which are not depleted in Eu show a large diversity in relative rare earth patterns, and tend to be low in ΣREE. They are not even consistent in Eu distributions, since some of the samples have chondritic relative Eu abundances and some show large enrichments in Eu relative to chondrites.

Rare earth fractionation in the sedimentary cycle

Since the main object of this study is to look for variations in sedimentary rare earth patterns that reflect differences in upper crustal composition, it is important to identify variations which are due to other causes. One possible cause of such variations is fractionation of the rare earth elements during the sedimentary cycle. It was noted in the preceeding discussion that, with only two exceptions, the samples depleted in Eu show very little diversity in relative rare earth distribution. Samples CL3 and CL4 were found to have anomalously low ΣLREE/ΣHREE and ΣREE. The shale normalized rare earth patterns (Fig. 4.16) of these samples show that the rare earths are progressively depleted with decreasing atomic number. Do these rare earth patterns reflect the composition of the source rocks, or are they due to some

other process such as weathering? The question deserves detailed consideration, because it is of fundamental importance to this study.

During the course of this project it was observed that a strong coherence exists between the elements La and Th in sedimentary rocks. The same strong coherence does not exist between Th and any of the heavy rare earths. A survey of La/Th ratios in igneous rocks produced a range of 1.8 to 18, with felsic rocks having generally low ratios and mafic rocks the higher ratios (Table 5.1). The sediments analyzed in this study (excluding the volcanic greywackes from the Baldwin Formation) have La/Th ratios averaging 2.8 $\pm$ 1.1. This is about that expected from a mixture of mainly felsic igneous rocks with a smaller amount of mafic rocks. Fig. 5.1 shows La plotted against Th for the sedimentary rocks. The most obvious deviations from the main trend are shown by samples CL3, CL4 and KH41. These three samples show extremely low La/Th ratios. These low La/Th ratios may not reflect a source rock composition, since igneous rocks depleted in La usually show an even greater depletion in Th. The low La/Th ratios suggest that either La has been removed or Th enriched in these samples during the sedimentary cycle. The low ΣLREE/ΣHREE and ΣREE of these samples suggest that it is a removal of La rather than an enrichment of Th that has occurred. Thus, it seems possible that the light rare earths were selectively removed from these samples in the sedimentary cycle.

Ronov et al. (1967) investigated the behaviour of the rare earths during weathering. When clastic material is exposed to weathering in a humid environment, acid conditions predominate in the extreme upper zone (soil) and alkaline conditions exist throughout the lower part. Ronov et al. (1967) found that the light rare earths are selectively removed in the acid zone, and accumulation and enrichment of the light rare earths takes place in the alkaline zone. This process operated in

Table 5.1 La/Th ratios in some igneous rocks

Sample	La (ppm)	Th (ppm)	La/Th
PCC-1 (peridotite)[1]	0.15	0.01	15
oceanic tholeiite[2]	1.8	0.10	18
W-1 (diabase)[1]	9.8	2.4	4.1
BCR-1 (basalt)[1]	26	6.0	4.3
AGV-1 (andesite)[1]	35	6.4	5.5
GSP-1 (granodiorite)[1]	191	104	1.8
G-1 (granite)[1]	101	50	2.0

[1] Flanagan, 1973.

[2] Robinson and Whitford, 1974.

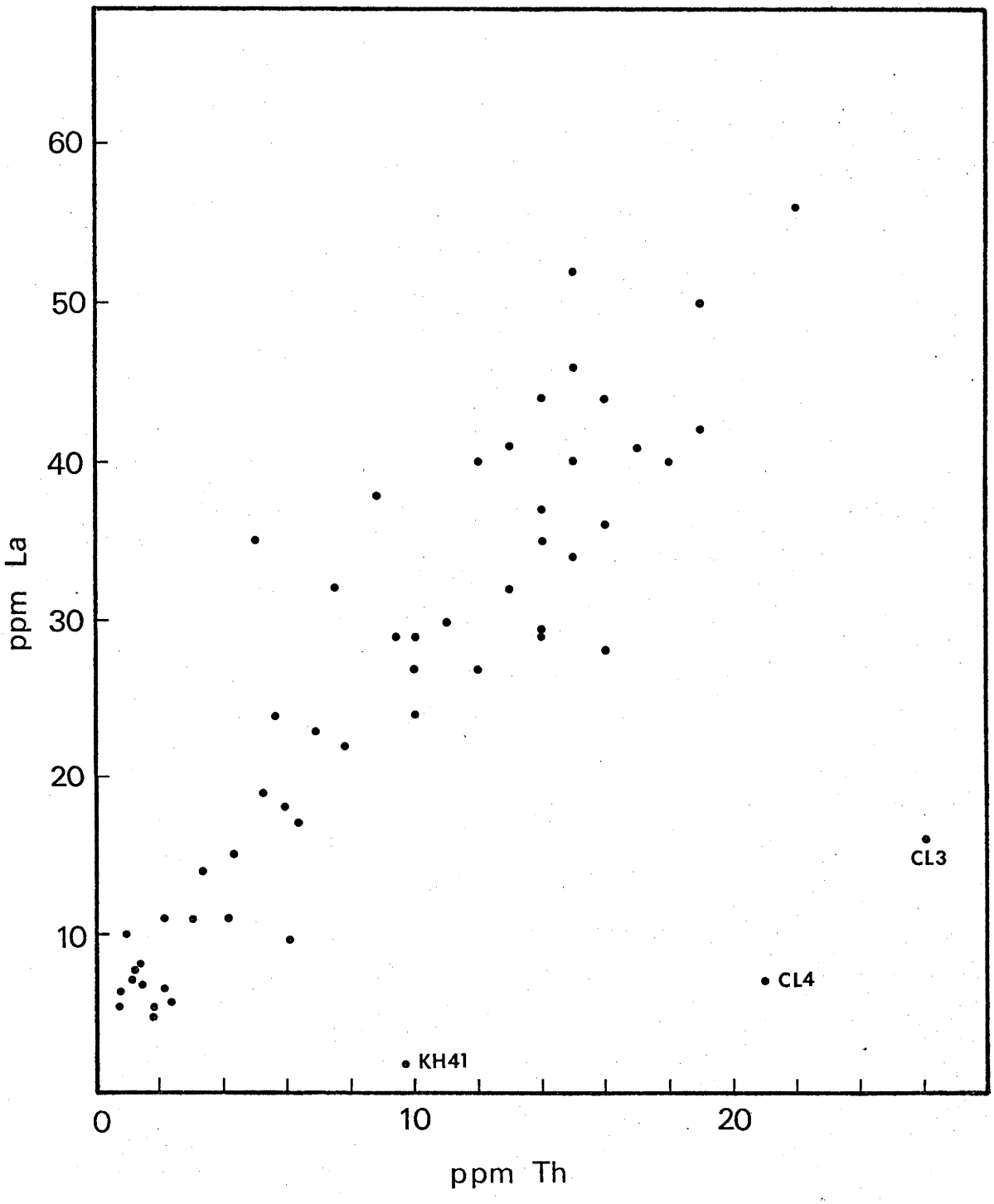

Fig. 5.1 The relationship of La to Th for the sedimentary rocks.

humid continental environments, but was not important in marine and arid environments. Samples CL3 and CL4 are from the Wogatti Sandstone of the Carnarvon Basin. This formation was deposited under marine conditions in the Upper Jurassic during a marine transgression over the eastern part of the Carnarvon Basin (Brown et al., 1968). The sea withdrew at the end of the Jurassic leaving the formation exposed in a non-marine environment, and during the Lower Cretaceous it was folded and eroded. Thus the Wogatti Sandstone was probably exposed to weathering in a continental environment during part of the Cretaceous, until another marine transgression in the Lower Cretaceous covered the area with fresh deposits of sediment. Samples CL2, CL3 and CL4 were taken near the top of the Wogatti Sandstone from cores from the Learmonth No. 2 well (Pudowskis, 1964). CL2, CL3, and CL4 were taken at 3 ft. intervals in the core in that respective order from the top. CL2 is a hard siliceous siltstone (89% SiO_2) containing large veins of amorphous silica. This sample seems enriched in ΣREE (179 ppm), considering that it is composed of more than70% amorphous silica. ΣLREE/ΣHREE (12.4) is also somewhat higher than the average sediment. CL3 is an alumina rich (26% Al_2O_3), silty mudstone, containing poorly sorted sand sized detritus. CL4 is a silty mudstone, enriched in both iron and alumina (20% Al_2O_3, 21% Fe_2O_3; Table 2.8), and containing abundant pisolitic siderite, which shows some alteration to hematite. Both CL3 and CL4 are extremely depleted in alkalies (<0.35%K_2O, <0.2%Na_2O), and enriched in Ti relative to other sediments analyzed in this study.

The composition and spatial relationship of CL3 and CL4 suggest that they are part of a "fossil" soil profile. Residual soils formed by weathering in a humid, stable environment are characterized by a strong zonation in composition (Pettijohn, 1957). The effect of acid leaching

by groundwater under these conditions is the removal of less resistant elements (Na, K, Ca etc.) while the more chemically resistant elements such as Al, Ti and Si are concentrated. Iron is usually oxidized to Fe^{3+} and precipitated as ferric oxides and hydroxides. Under extreme weathering conditions even Si is removed, leaving the residue enriched in Al, Ti, and Fe. Such a soil usually consists of an uppermost zone rich in Al, and below that a zone rich in Al and Fe (Valeton, 1972; Hunt, 1972).

If the soil later becomes waterlogged (usually after burial), reducing conditions may develop. Under these conditions ferric iron is dissolved and precipitated as siderite or even pyrite in the iron rich zone (Valeton, 1972).

The sharp change in composition between CL2 and CL3 possibly represents a disconformity between the Wogatti Sandstone and the overlying strata. This is consistent with the interpretation of CL3 and CL4 as part of a fossil soil profile. Condon (1968) considered the high silica content of Cretaceous sediments such as the Windalia Radiolarite of the Carnarvon Basin to be due to run-off from a mature land surface weathering under a humid climate. The existence of lateritized erosion surfaces on some Cretaceous sediments in the Carnarvon Basin also indicates that conditions were warm and humid (Condon, 1968). There is ample evidence that fractionation of the rare earths can occur in soils weathered under these conditions. Gordon et al. (1958) reported that bauxitic clays are depleted in La relative to Y in comparison to their source rocks, and Ronov et al. (1967) reported the same effect. If the rare earths removed during weathering are precipitated with the silica removed in the same way, then that could account for the apparent enrichment of light rare earths and ΣREE in CL2.

The Archaean siltstone KH41 has many characteristics in common with CL3 and CL4; low ΣLREE/ΣHREE (3.5), low ΣREE (9 ppm), and low La/Th (0.19).

This sample is from the Gunga meta-argillites; part of the Mungari Beds which outcrop in a small area between Coolgardie and Kalgoorlie, W.A. (informal stratigraphic nomenclature after Glikson (1971a)). By analogy with CL3 and CL4 the sample shows evidence of alteration of its rare earth distribution in the sedimentary cycle. This possibility is considered in detail in the discussion of the Archaean sediments.

It is difficult to ascribe the unusual trace element chemistry of CL3, CL4 and KH41 to any cause other than fractionation in the sedimentary process. All of the other samples analyzed in this study fall broadly within the main trend in Fig. 5.1, which indicates the La/Th ratio may be very useful in predicting when alteration of the rare earths in the sedimentary cycle has occurred. Because the evidence suggests that CL2, CL3 and CL4 have not retained the rare earth distributions of their source rocks. they will not be considered in the remaining discussions.

Archaean sediments

Introduction

The Archaean rocks of the Eastern Goldfields of Western Australia comprise two distinct lithologies. The larger volume consists of acid intrusive rocks, with the remaining volume composed of greenstone successions, mostly syclinal in structure. The greenstone belts consist of ultramafic - mafic and felsic volcanic - clastic associations (Williams, 1970). The mafic volcanic rocks, which make up over fifty percent of the greenstones, are mainly low-K tholeiitic basalts (Hallberg, 1972). Ultramafic rocks, including peridotitic volcanics with spinifex textures, are common at lower stratigraphic levels (Nesbitt, 1971). Felsic volcanics of dacitic, rhyodacitic, and rhyolitic

compositions are abundant at higher stratigraphic levels, as are thick sequences of clastic sediments. The clastic associations contain abundant fragments from nearby lenses of felsic porphyries (Glikson, 1971a). Acid intrusive rocks of both sodium-rich and potassium-rich varieties are present. The more potassic intrusives are mainly adamellites, and are considered as younger than the greenstone sequences (Glikson, 1972; Compston and Turek, 1973). Age relationships of the more sodium-rich intrusives are less clear, but Glikson (1972) considers at least some of them to predate the clastic sequences. The clastic sediments are usually metamorphosed to the middle greenschist facies (Glikson, 1971a).

The Eastern Goldfields represent an Archaean granite-greenstone terrain. These curious crustal features have long been a subject of debate, and there are many theories as to their origin. Glikson (1971b), Glikson and Sheraton (1972), Glikson (1972), and Glikson and Lambert (1973) have proposed that the lowermost ultramafic-mafic assemblages of the greenstone belts are remnants of an ancient oceanic crust, which has undergone partial melting at the base to produce the observed sodium rich intrusive and felsic volcanic rocks. An earlier, and still popular, theory is that the greenstone belts developed on pre-existing sialic crust (Windley, 1973; Pettijohn, 1972; Sutton, 1973). Some proponents of this view, impressed by the very old ages obtained by radiometric dating of some Archaean high grade metamorphic terrains (McGregor, 1973; Bridgewater et al., 1973), consider the granite-greenstone terrains as structures formed by rifting in early crustal nuclei (Windley, 1973). A theory that has gained popularity in recent years is the uniformitarian view that Archaean greenstone belts are analogous to modern island arc systems (Wilson et al. 1965; Folinsbee et al., 1968; Hart et al., 1970; White et al., 1971; Anhaeusser, 1973; Gélinas and Brooks, 1973; Goodwin, 1973; Jakeš and Taylor, 1974; Jahn et al., 1974). Supporters

of this view have pointed out many similarities, chemical ones in particular, between rocks of Archaean greenstone belts and those of modern island arc systems. White et al. (1971) have shown that tholeiitic rocks in the Eastern Goldfields Province have some geochemical affinities to island arc tholeiites (Jakeš and Gill, 1970). Gélinas and Brooks (1973) pointed out that Archaean tholeiites have a wider range in chemistry (e.g. SiO_2) than modern ocean floor tholeiites are assumed to show. Jakeš and Taylor (1974) noted that the lack of Eu anomalies relative to chondrites in Archaean sediments reported by Wildeman and Haskin (1973) and Wildeman and Condie (1973) is consistent with the island arc analogy, since the major types of volcanic rocks associated with island arcs do not have Eu anomalies. Many workers have reported rocks of the calc-alkaline series in close association with tholeiitic rocks in the Canadian greenstone belts (Goodwin, 1973; Gélinas and Brooks, 1973; Jahn et al., 1974; Baragar and Goodwin, 1969; Folinsbee et al., 1968; Baragar, 1966). In the discussion which follows, I will consider the rare earth patterns of Archaean sediments from the Kalgoorlie area, and their implications for crustal development in the region in the light of the various theories outlined above. The samples were described in chapter two, and their rare earth patterns were presented in chapter four.

Eu anomalies

As noted earlier, the Archaean sediments analyzed in this study are enriched in Eu relative to the younger sediments and the NASC. Six of the Archaean sediments even have significant enrichments of Eu relative to chondrites. Neither the tholeiitic or calc-alkaline rock associations in modern island arcs normally show significant enrichments in Eu relative to chondrites (Philpotts et al., 1971; Gill, 1970; Gorton, 1974). Does this jeopardize the conclusion of Jakeš and Taylor (1974), that the

relative Eu abundance in Archaean sediments is consistent with that of island arc volcanic rocks? In order to examine the behaviour of Eu (and the other rare earths) during the sedimentary cycle in material of purely volcanic parentage, a suite of Devonian volcanic greywackes was analyzed (Table 2.5). A petrological study of these greywackes was made by Chappell (1968), and they were found to have calc-alkaline andesitic compositions. These rocks contain very little detrital quartz or sedimentary rock fragments, indicating they were formed almost exclusively of detritus from andesitic volcanoes within the New England Geosyncline (Brown et al., 1968; Chappell, 1968). The major element chemistry shows that these rocks have undergone very little alteration except for an enrichment in sodium, which is commonly observed in volcanic sediments of this type (Pettijohn et al., 1972). Therefore, it was expected that these greywackes would retain the rare earth distribution of their parent rocks, which are believed to be calc-alkaline andesites. On that basis, it would be predicted that the greywackes would show no Eu anomalies relative to chondrites. Five of the greywackes, as expected, show no significant Eu anomaly relative to chondrites, but two samples (M284, M285) have large enrichments of Eu ($Eu/Eu^* \sim 1.5$) relative to chondrites (Table 4.6; Figs. 4.10 and 4.11). This is comparable to the largest enrichments in Eu observed in the Archaean sediments (see Table 4.2). The overall rare earth patterns of the greywackes are consistent with their being derived from calc-alkaline island arc rocks. Calc-alkaline rocks from island arcs show a good correlation between K_2O and $\Sigma LREE/\Sigma HREE$ (Taylor et al., 1969; Gorton, 1974). The low values of $\Sigma LREE/\Sigma HREE$ (2.7 - 5.2) in the greywackes are in accord with their low K_2O contents (0.30 - 0.94%). Thus, the Devonian greywackes demonstrate two points. (1) Sediments derived from rocks without a negative Eu anomaly do not develop a negative Eu anomaly in the sedimentary cycle, at least not

under the weathering conditions that produced these greywackes.
(2) Positive Eu anomalies relative to chondrites are not unique to Archaean sediments, but seem to develop during the weathering and deposition of sediments produced from at least certain kinds of volcanic rocks.

It is possible that a chemical effect during weathering could be responsible for the enrichment in Eu relative to the other rare earths, but no mechanism for this is known at the present time. However, there is a simple mechanism which could explain the enrichment in Eu. It is well known that the feldspars are the only important rock forming minerals that are normally enriched in Eu relative to the other rare earths. In many types of volcanic rocks plagioclase is by far the dominant phenocryst phase. Plagioclase is also more resistant to decomposition by weathering than the ferromagnesian minerals and glassy groundmass. During weathering the plagioclase phenocrysts could be mechanically separated from some of the groundmass which is more quickly decomposed by chemical weathering. In this way plagioclase could become concentrated by mechanical sorting, and the resulting sedimentary rocks may show an enrichment in Eu relative to their source rocks. Among the Baldwin greywackes analyzed in my study only in sample M285 are plagioclase fragments predominate over rock fragments (Chappell, 1968). CIPW norms reported by Chappell (1968) also show that samples M285 and M284 have a higher normative plagioclase content than any of the other greywackes.

Thus, the enrichment in Eu of these two samples seems to be related to plagioclase content, as expected from the above argument. Since most of the greywackes are not enriched in Eu relative to the presumed source rocks, it is probable that this is not an important process on a large scale. It may however, explain variations in Eu/Eu* in a particular formation.

Whatever the reason, it seems clear that the enrichment in Eu relative to chondrites in some Archaean sediments does not indicate that Eu was relatively more abundant in the Archaean crust in general, because the same effect is observed in some younger sediments. The fact that this effect has only been observed in the volcanic sediments does support the contention of Jakeš and Taylor (1974) that the Archaean sediments were mainly derived from volcanic rocks.

Sediments depleted in the heaviest rare earths

The Archaean sedimentary rock KH21, and to a lesser extent KH30 and KH32, are depleted in the heaviest rare earths. In this respect, they are distinctly different from any of the other sediments analyzed in this study. This feature is best developed in KH21, so that sample only will be referred to in the following discussion. KH21 is a shale from the Gundockerta Formation of the association IV of Williams (1970). The sample was taken from an outcrop southeast of Kalgoorlie, W.A. The clastic sediments of the Gundockerta Formation are mainly associated with felsic volcanic rocks (Williams, 1970). The rare earth pattern of KH21 (Fig. 5.2) is reminiscent of those of Archaean tonalite, trondhjemite, and dacite from an Archaean granite-greenstone terrain in Minnesota - Ontario reported by Arth and Hanson (1972). These patterns were thought to be due to partial melting of quartz eclogite or amphibolite of basaltic composition at upper mantle depths, leaving a residue containing garnet and pyroxene. Garnet has the well known property of concentrating the heaviest rare earths relative to the light rare earths to a more extreme degree than any other major rock forming mineral (Schnetzler and Philpotts, 1970). Thus, a melt in equilibrium with a garnet bearing residue will be highly depleted in the heaviest rare earths. T. Green and Ringwood (1968) demonstrated that a liquid of andesitic composition results from the partial melting of a quartz

eclogite under dry conditions, and under wet conditions the liquid is rhyodacitic. The rare earth pattern shown by KH21 strongly suggests that garnet was a residual phase during melting or fractional crystallization. The presence of garnet as a stable phase indicates that melting took place at deep levels. This could occur on a sinking slab of basaltic material such as in modern island arc systems or at the base of a thick pile. What type of rocks were responsible for the rare earth pattern of KH21? The close spatial relationships as well as compositional similarities indicates that the felsic volcanics were major source rocks for the clastic sediments in the Kalgoorlie area (Williams, 1970; Glikson, 1971a). From the data of Arth and Hanson (1972) it might be predicted that the felsic volcanics and sodium rich felsic intrusive rocks of the Kalgoorlie area have heavy rare earth depleted patterns similar to KH21. To determine if this is so, a sample of the Kambalda Granite was analyzed. The Kambalda Granite is a sodium rich acid pluton near Kamblada, W.A. in the region southeast of Kalgoorlie. The major element chemistry and mineralogy were reported by Roddick (1974). The chondrite normalized rare earth pattern of the Kambalda Granite is shown in Fig. 5.2, along with that of KH21. The patterns are nearly parallel, but the abolute rare earth abundances of KH21 are about twice those of the Kambalda Granite. This is consistent with the differences in K_2O contents for these rocks, which are 2.2% for the Kambalda Granite and 4.3% for KH21. Despite the differences in absolute abundances, the rare earth pattern of the Kambalda Granite shows the same depletion of heavy rare earths shown by KH21, suggesting a similar origin for the source rocks of KH21 and the Kambalda Granite. Similar rare earth patterns have been reported for Archaean felsic volcanic rocks by Condie and Baragar (1974) and Jahn et al. (1974), indicating that they are closely related to the sodic intrusives.

It appears that KH21 was derived almost exclusively from the

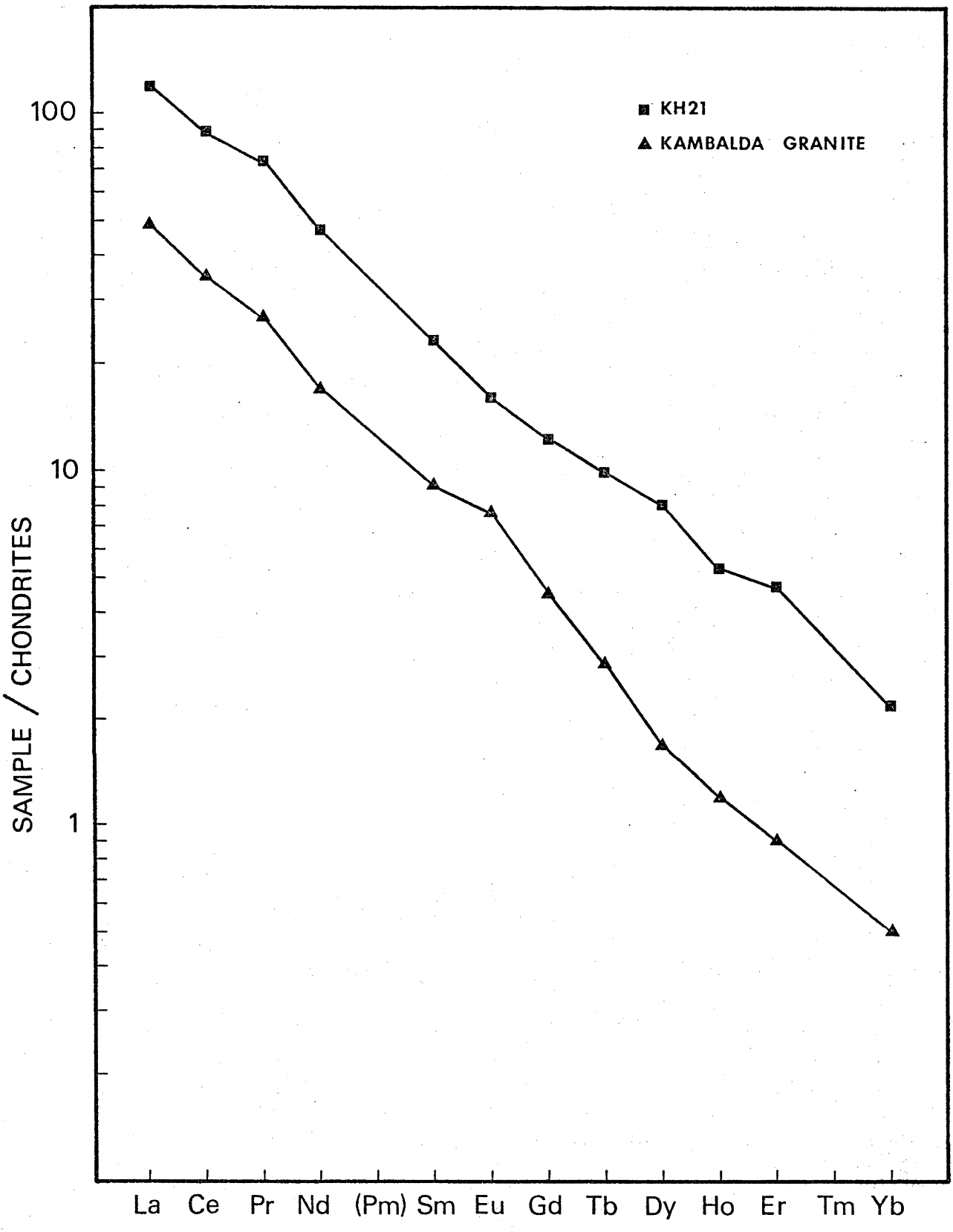

Fig. 5.2 Rare earth patterns for the Kambalda Granite and an Archaean sedimentary rock from the Kalgoorlie area.

felsic rocks. The ubiquitous low-K tholeiites in Archaean greenstone belts have nearly flat rare earth patterns relative to chondrites (White et al., 1971; Jahn et al., 1974), so that even a small contribution from the tholeiites would have raised the abundances of the heaviest rare earths in KH21. The absolute abundances of rare earths in KH21 are considerably greater than those in either the Kambalda Granite or the rocks of Arth and Hanson (1972), but are similar to those in Archaean andesites, dacites, and rhyodacites from the South Pass (Wyoming) and Barberton (S. Africa) greenstone belts (Condie and Baragar, 1974).

Perhaps the most persuasive argument used by supporters of the island arc anology has been that rocks of the tholeiitic and calc-alkaline suites are associated in Archaean greenstone belts in much the same way as in modern island arcs (Wilson et al., 1965; Goodwin, 1973; Jahn et al., 1974). Most reports of calc-alkaline rock occurrences in greenstone belts have come from the North American belts. Hallberg (1972) did not find evidence of rocks with calc-alkaline chemistry in the Eastern Goldfields Province of Western Australia. White et al. (1971), in noting the apparent absence of calc-alkaline rocks in the area, suggested that they may have been destroyed through weathering and might possibly be recognized in the sediments.

Published rare earth data on rocks from Archaean greenstone belts which are of the type claimed to be of the island arc calc-alkaline association, have shown that these rocks are depleted in the heaviest rare earths in much the same way as KH21. Andesites, dacites, and rhyodacites from the South Pass greenstone belt (Wyoming) and the Barberton greenstone belt (S. Africa) show rare earth patterns very similar to that of KH21 in both relative and absolute abundances (Condie and Baragar, 1974). Jahn et al. (1974) considered rare earth patterns of this type to be indicative of the calc-alkaline chemistry of their

rocks, and to support the island arc analogy. Jahn et al. (1974) cited the model of T. Green and Ringwood (1968) for the genesis of the calc-alkaline rock suite as support for this interpretation. As noted earlier, the work of T. Green and Ringwood (1968) demonstrated that rocks of calc-alkaline chemistry could be produced by partial melting of quartz eclogite, leaving a garnet bearing residue. This model predicts a large depletion of the heaviest rare earths in the melt, because of the residual garnet, and so could explain the observed rare earth patterns of these Archaean rocks. However, the calc-alkaline rocks of modern island arcs are not highly depleted in the heaviest rare earths as predicted by this model. Rare earth patterns are one of the most diagnostic features of island arc calc-alkaline rocks. These rocks have a variable enrichment of the light rare earths, usually related to K_2O content, and a less inclined, often nearly flat, heavy rare earth pattern relative to chondrites (see Taylor et al., 1969; Gorton, 1974). This appears to be one of the main difficulties with the model of T. Green and Ringwood (1968) as a mechanism for directly producing island arc calc-alkaline rocks. More recent models have favoured a more complex interaction between slab melt and overlying mantle (Nicholls and Ringwood, 1973; Stern and Wyllie, 1973; Ringwood, 1974; Nicholls, 1974). In this way the rare earth distribution of melt from the downgoing slab of oceanic crust is presumably modified to produce the distribution observed in island arc calc-alkaline rocks. Thus, there is evidence for a basic genetic difference between the Archaean rocks for which rare earth data is available and the calc-alkaline rocks of modern island arcs.

Sediments depleted in the light rare earths

The other Archaean sediments (KH1, KH36, KH37, KH38, KH44, KH47) have rare earth patterns much more consistent with those of modern day

island arc calc-alkaline rocks, and so they deserve a more detailed comparison. These sediments are depleted in the light rare earths relative to the NASC and the younger sediments of my study, as are most calc-alkaline volcanics. A comparison was made with a medium K calc-alkaline andesite (K_2O = 2.2%) from Indonesia (D.J. Whitford, unpublished data), which is considered to be typical of its rock type in Indonesia (Whitford, pers. comm.). Fig. 5.3 is a plot of trace elements in the calc-alkaline volcanic versus the same elements in KH38. Fig. 5.4 is a comparison of the chondrite normalized rare earth pattern of the calc-alkaline rock with those of KH38 and KH44. It is clear from Figs. 5.3 and 5.4 that these sediments have remarkable geochemical affinities with the calc-alkaline rock. The implication seems to be that these sediments were derived from calc-alkaline rocks of the type found in modern island arcs. This would be an important point in favour of the island arc analogy to the Western Australian greenstone terrains. However, there is another possibility which may explain the trace element abundances of these sediments. The sediments in the Kalgoorlie area were described as a mixture of the felsic porphyries and mafic greenstones by Glikson (1971a), on the basis of petrographic and chemical evidence. Ojakangas (1972) found that the Archaean clastic sediments in the Vermilion greenstone belt (Minnesota-Ontario) were derived primarily from felsic volcanics and, to a lesser degree, the greenstones. Arth and Hanson (1972) found the rare earth pattern of an Archaean greywacke from the same area to be consistent with a mixture of greenstone (low-K tholeiite) and rocks depleted in the heaviest rare earths.

As described earlier, KH21 seems to have been derived almost exclusively from the felsic volcanics and/or sodic plutonic rocks which are depleted in the heaviest rare earths. Perhaps a mixture of those rocks and the greenstones are responsible for the rare earth patterns

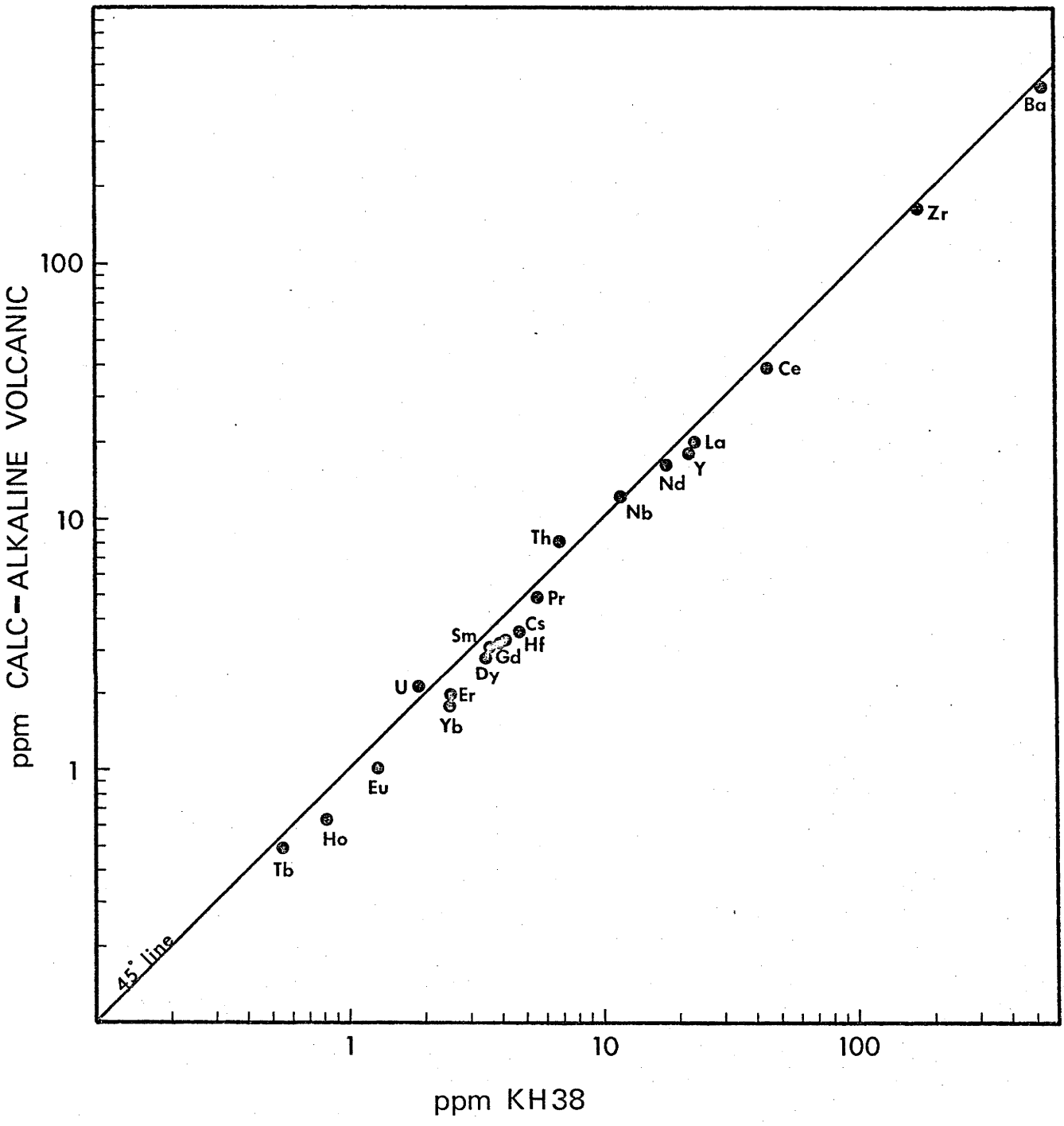

Fig. 5.3 Comparison of trace element data between a calc-alkaline volcanic rock from Indonesia and an Archaean sedimentary rock from the Kalgoorlie area.

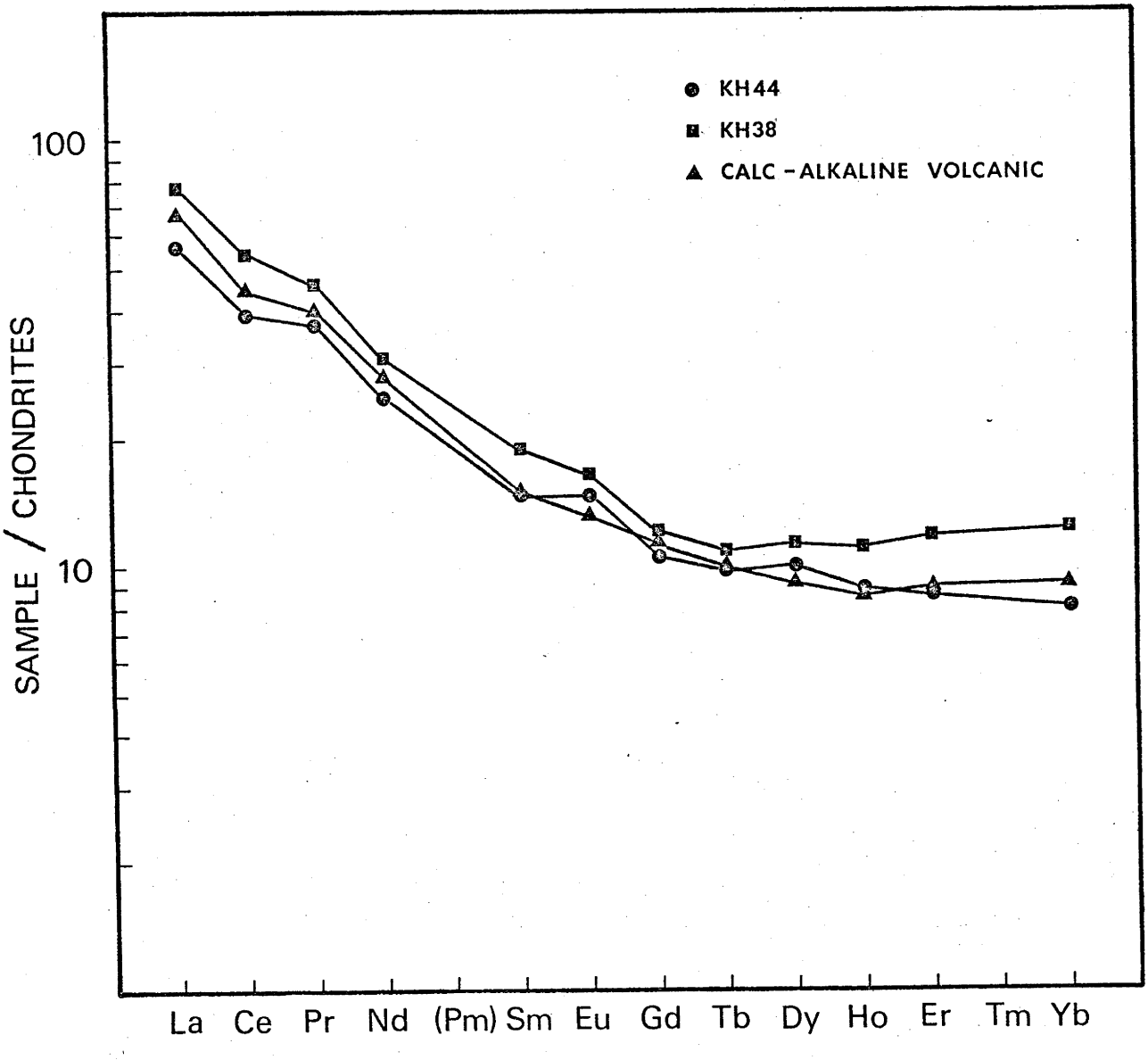

Fig.5.4 Rare earth patterns for a calc-alkaline volcanic rock from Indonesia and two Archaean sedimentary rocks from the Kalgoorlie area.

of the remaining Archaean sediments. The greenstones are mostly low-K tholeiitic basalts (Glikson, 1970; Hallberg, 1972), and as such have a nearly flat chondrite normalized rare earth pattern (White et al., 1971; Jahn et al., 1974). Absolute rare earth abundances of low-K tholeiites of the types found in the ocean floor and island arc environments vary between about 5 and 25 x chondrites, values between 10 and 20 being most common (Philpotts et al., 1971; Jakeš and Gill, 1970; Robinson and Whitford, 1974; White et al., 1971; Kay et al., 1970). KH21 probably represents a mixture of the felsic rocks, and so it can be used as an estimate of the average composition of rocks of this type in the Kalgoorlie area. Mixing calculations were carried out using the elemental abundances of KH21 and a hypothetical low-K tholeiite, with a flat rare earth pattern and absolute abundances of 15 x chondrites, as end members. Fig. 5.5 is a plot of trace-element abundances in KH38 versus those in a mix of 50% KH21 and 50% low-K tholeiite. Fig. 5.6 shows a comparison of the chondrite normalized rare earth patterns of KH38 and KH44 with that of the above mix. As can be seen from Figs. 5.5 and 5.6, the trace element abundances of these sediments can be derived from a mixture of the felsic rocks and the tholeiites.

There is considerable evidence that this is indeed the way in which the sediments were derived. Tholeiitic basalts and felsic volcanics (dacites, rhyodacites) are abundant in the Kalgoorlie area, and the latter are usually associated with the clastic sediments (Williams, 1970; Kriewaldt, 1969; Glikson, 1971a; Hallberg, 1972). It would be surprising if sediments derived by weathering in this terrain did not contain a large component from these two very abundant rock types. Several studies of Archaean sediments have shown that they are commonly a mixture of these rock types (Glikson, 1971a; Hanson and Goldich, 1972; Ojakangas, 1972; Arth and Hanson, 1972).

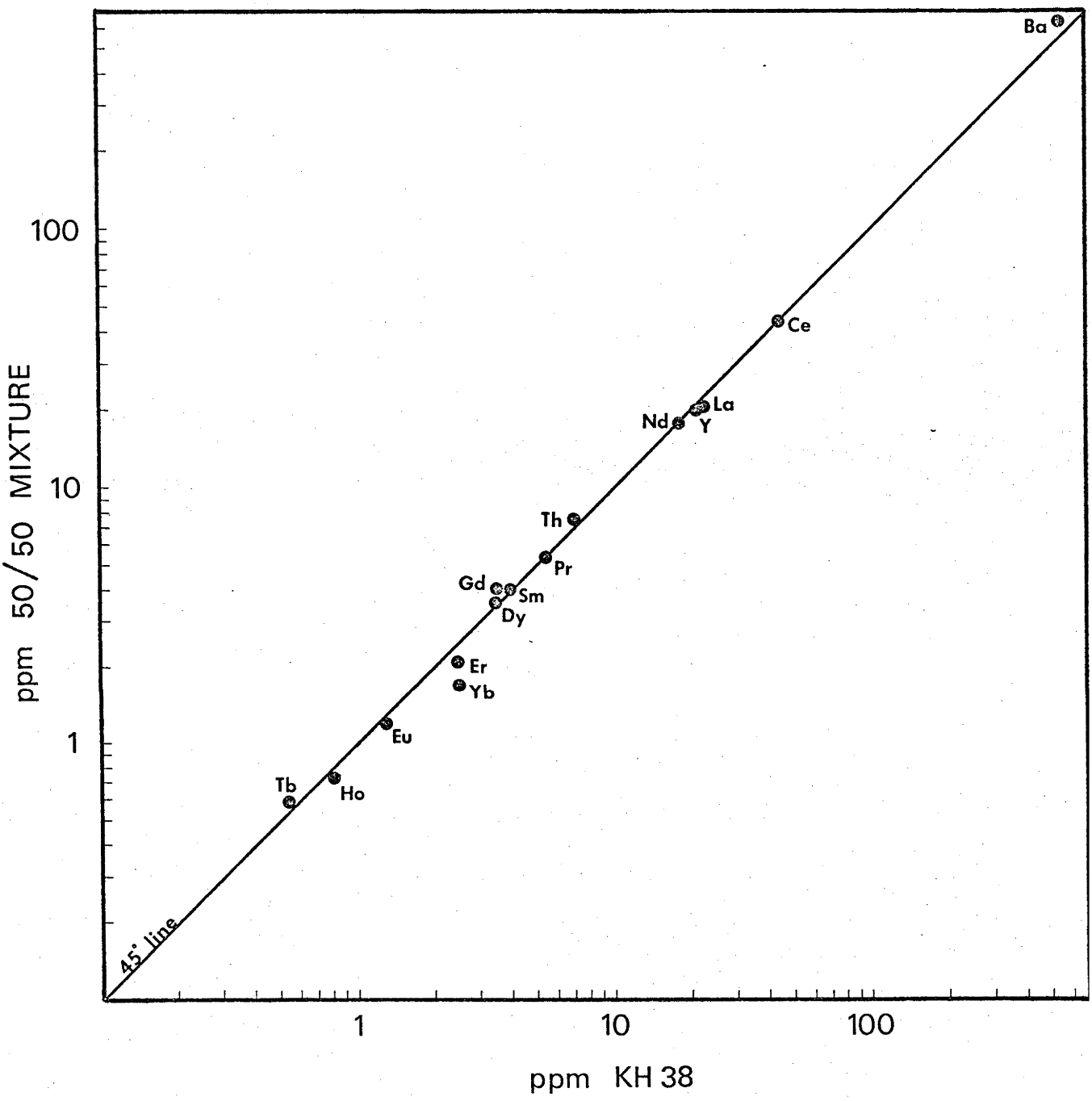

Fig. 5.5 A plot of trace element abundances of KH38 vs. those in a 1:1 mixture of KH21 and a hypothetical low-K tholeiite with rare earth abundances of 15 x chondrites.

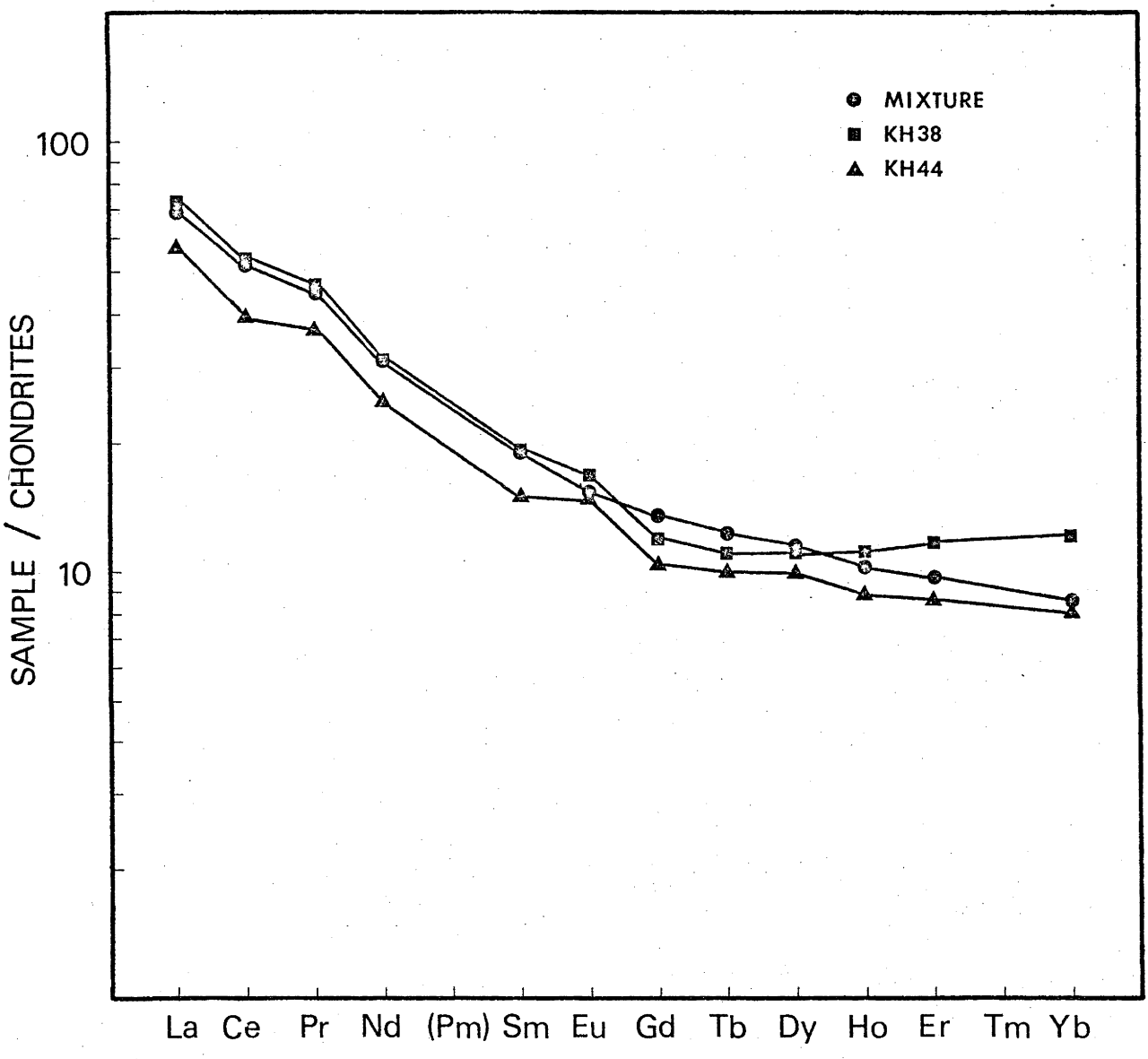

Fig. 5.6 A comparison of the chondrite normalized rare earth patterns of KH38 and KH44 with that of the 1:1 mixture of KH21 and hypothetical tholeiite.

Intermediate rocks (andesites) are rare in the Kalgoorlie area (Hallberg, 1972; Williams, 1973), and, as noted earlier, those from other Archaean terrains for which data is available show patterns depleted in the heaviest rare earths to a similar degree as KH21.

The trace element affinities of the Archaean sediments KH1, KH36, KH37, KH38, KH44 and KH47 to island arc calc-alkaline rocks appears to be due to the ability of mixtures of Archaean tholeiitic and felsic rocks to produce a calc-alkaline trace element distribution. It is interesting to consider possible reasons for this. In some recent models for genesis of the island arc calc-alkaline suite, subducted oceanic crust is seen as being converted to a quartz eclogite at depth and partially melting as the temperature reaches the solidus (T. Green, 1972; Nicholls and Ringwood, 1973; Stern and Wyllie, 1973; Ringwood, 1974; Nicholls, 1974). This melt, for reasons already discussed, will probably have a rare earth distribution similar to that of KH21. Nicholls and Ringwood (1973), Ringwood (1974) and Nicholls (1974) have suggested that such a melt would probably not reach the surface directly, but would react with the overlying mantle to form a garnet pyroxenite. Diapirs of the pyroxenite could then rise and undergo partial melting to produce the calc-alkaline suite. Stern and Wyllie (1973) concluded that partial melts of subducted oceanic crust could not directly produce the calc-alkaline rocks of island arcs, but may mix with melts of the overlying mantle to produce these rocks. Partial melting of the mantle under wet conditions has been suggested as the mechanism responsible for the island arc tholeiitic suite (Nicholls and Ringwood, 1973). Thus, in the mechanism discussed by Stern and Wyllie (1973), the two end members used in the mixing calculations for Figs. 5.5 and 5.6 may be involved. Mixing of these two components has a remarkable ability to reproduce even the fine details of calc-alkaline rare earth patterns. For instance, when rare earth

patterns for low-K and high-K calc-alkaline rocks are plotted together, they sometimes are seen to cross in about the middle of the pattern i.e. rocks with higher abundances of the light rare earths are more depleted in the heaviest rare earths than are rocks less enriched in light rare earths (see data in Taylor et al. (1969) and Gorton (1974)). Varying the relative amounts of the two end members in the mixing calculation above will produce this same effect, and to about the same degree.

KH41

In a previous section of this chapter, it was noted that the trace element chemistry of the Archaean siltstone KH41 showed evidence of alteration in the sedimentary cycle. ΣRÈE, ΣLREE/ΣHREE, and La/Th were similar to those in samples believed to be residual soils formed by weathering in a stable, humid environment. However, there is no other evidence that KH41 was subjected to acid weathering, and its major element chemistry (high SiO_2, high K_2O) suggests that it was not. Thus, other reasons for the unusual trace element chemistry of this sample must be sought.

KH41 is a siliceous siltstone from the low stratigraphic levels (Gunga meta-argillites) of the Mungari Beds (informal stratigraphic terms after Glikson (1971a)). These sediments overlie mafic and ultramafic rocks of the Coolgardie Ophiolites (Glikson, 1971a).

The major element chemistry and stratigraphic position of KH41 are remarkably similar to those of Archaean siliceous aluminous schists which overlie basaltic komatiites in the Theespruit Formation of the Onverwacht Group, S. Africa. Table 5.2 compares the major element chemistry of KH41 with that of the average siliceous aluminous schist of the Theespruit Formation reported by Anhaeusser (1971b). Recent work on the trace element chemistry of rocks from the Onverwacht Group has shown that some siliceous aluminous schists of the Theespruit

Table 5.2 Comparison of siliceous sediments from the lower stratigraphic levels of the Onverwacht Group (S. Africa) and the Kalgoorlie area.

	KH41 Gunga meta-argillite, Kalgoorlie area	Average silica-alumina schist[1] Theespruit Formation
SiO_2	78.00	78.91
TiO_2	0.24	0.54
Al_2O_3	14.35	15.14
Fe_2O_3*	0.98	1.02
MgO	0.67	0.38
CaO	0.03	0.29
Na_2O	0.09	0.40
K_2O	3.07	2.67
MnO	-	0.01
P_2O_5	0.01	0.15

* Total Fe as Fe_2O_3

1 Average siliceous aluminous schist, Jamestown Schist Belt, Barberton area (Anhaeusser, 1971a).

Formation have the same characteristic trace element chemistry as KH41, including low La/Th, ΣLREE/ΣHREE, and ΣREE (Taylor and Glikson, in prep.). Viljoen and Viljoen (1969a) considered these rocks to result from alteration of felsic pyroclasts. They are associated with cherts, minor felsic porphyries, and some small barite deposits (Viljoen and Viljoen, 1969b). These authors considered the possibility that alteration was accomplished by acid surface weathering, but concluded that a subaqueous origin was more probable. Hydrothermal emanations from late stage volcanic activity was considered a likely weathering agent.

In my opinion, the major element and trace element chemistry of KH41 and the Theespruit schists are consistent with derivation by either of two mechanisms. (1) Alteration of felsic material by a weathering process which selectively removed many elements, including the rare earths, through incongruent dissolution, leaving a residue rich in silica and alumina. Potassium could have been restored by reaction with the environment, presumably sea water, to form micaceous minerals (sericite is a common mineral in these rocks). Acid weathering would normally lead to a depletion in potassium, but alkaline conditions in a marine environment favour the restoration and retention of potassium (Pettijohn, 1957). Th, highly insoluble, would be retained, leading to low La/Th ratios. It may be possible to test this mechanism in the Theespruit Formation, since the rare earths removed in this way may have precipitated with silica to form the cherts which overlie the schists. (2) Weathering of ultramafic or mafic rocks under marine conditions could have led to the enrichment of sea water in various elements, the more insoluble of which were eventually precipitated to form the siliceous aluminous material as well as the associated chert and barite. The rare earth pattern of KH41 is consistent with this mechanism, and could even represent an enrichment in rare earths if an ultramafic parent is assumed.

Both mechanisms require fractionation between the light and heavy rare earths in order to achieve the observed rare earth pattern of KH41. Considering the overall chemistry of these rocks, I regard felsic rocks as the most likely source material but the evidence is certainly not conclusive.

Several writers have commented on the stratigraphic similarities between the Eastern Goldfields of Western Australia and the Barberton Mountain Land of South Africa (e.g. Viljoen and Viljoen, 1969c; Anhaeusser, 1971a). The striking similarities, both compositional and spatial, between KH41 and the siliceous aluminous schists of the Theespruit Formation, suggests that the source rock composition and environment of weathering and deposition were nearly the same for both. This is another indication of the close parallel development of the two regions.

Rare earth distribution and stratigraphic position

The stratigraphy of the area around Kalgoorlie has been discussed by Woodall (1965), Kriewaldt (1969), Williams (1970, 1973), and Glikson (1970, 1971a). The most prominent feature of the area is the Kurrawang Syncline, a thick clastic sequence bordered on the west by mafic and ultramafic rocks of the Coolgardie Belt and on the east by mafic and ultramafic rocks of the Kalgoorlie Belt. The area east of the Kalgoorlie Belt is occupied by another thick clastic sequence similar in part to the Kurrawang sequence (Glikson, 1970). Interpretation of the detailed stratigraphy is open to debate. Kriewaldt (1969) considered the Coolgardie and Kalgoorlie Belts to be a single structural layer, folded to form the base of the felsic-clastic sequence in the Kurrawang Syncline. Glikson (1971a) maintained that the Coolgardie Belt represented a lower and thus older structural layer than the Kalgoorlie belt. Glikson considers the sedimentary sequence in the Kurrawang Syncline to consist of two major units, one

which overlies rocks of the Coolgardie Belt (lower Mungari Beds) and is in turn overlain by a mafic-ultramafic layer equivalent to the Kalgoorlie Belt, and an upper clastic sequence (upper Mungari Beds, Kurrawang Beds) which overlie that sequence. Glikson places the clastic sequence east of the Kalgoorlie Belt as equivalent to the upper clastic sequence in the Kurrawang Syncline. The most detailed stratigraphic model of the area has been proposed by Williams (1970). Williams views the area as consisting of two discrete volcanic cycles. Each cycle is composed of a mafic-ultramafic association (Associations I and III) overlain by a felsic-clastic association (Associations II and IV). The two volcanic cycles are separated by a possible unconformity. Glikson (1971a) correlated the sequence across the Kurrawang syncline to the rock associations of Williams in the following way: Coolgardie Belt (Association I); lower Mungari Beds (Association II); upper Mungari Beds and Kurrawang Beds (Association IV); Kalgoorlie Belt (Association III). Both authors place the clastic sequence east of the Kalgoorlie belt in Association IV.

Fig. 5.7 shows the sampling locations for the Archaean sediments analyzed in this study. Samples KH44 and KH47 were taken in the Coolgardie Belt, KH41 in the lower Mungari Beds (Gunga meta-argillites), KH30 and KH32 in the upper Mungari and Kurrawang Beds, KH1, KH36, KH37 and KH38 in the Kalgoorlie Belt, and KH21 in the clastic sequence (Association IV) east of the Kalgoorlie Belt. The sediments show an obvious trend in rare earth distribution with position in the sequence. Samples from the felsic-clastic association IV (KH21, KH30, KH32) are depleted in the heaviest rare earths (average ΣLREE/ΣHREE = 15), reflecting their predominantly felsic source. Samples in or near the mafic-ultramafic sequences in the Coolgardie and Kalgoorlie Belts (KH1, KH36, KH37, KH38, KH44, KH47) are more enriched in the heavy rare earths (average ΣLREE/ΣHREE = 6.3), suggesting that they contain a higher mafic component.

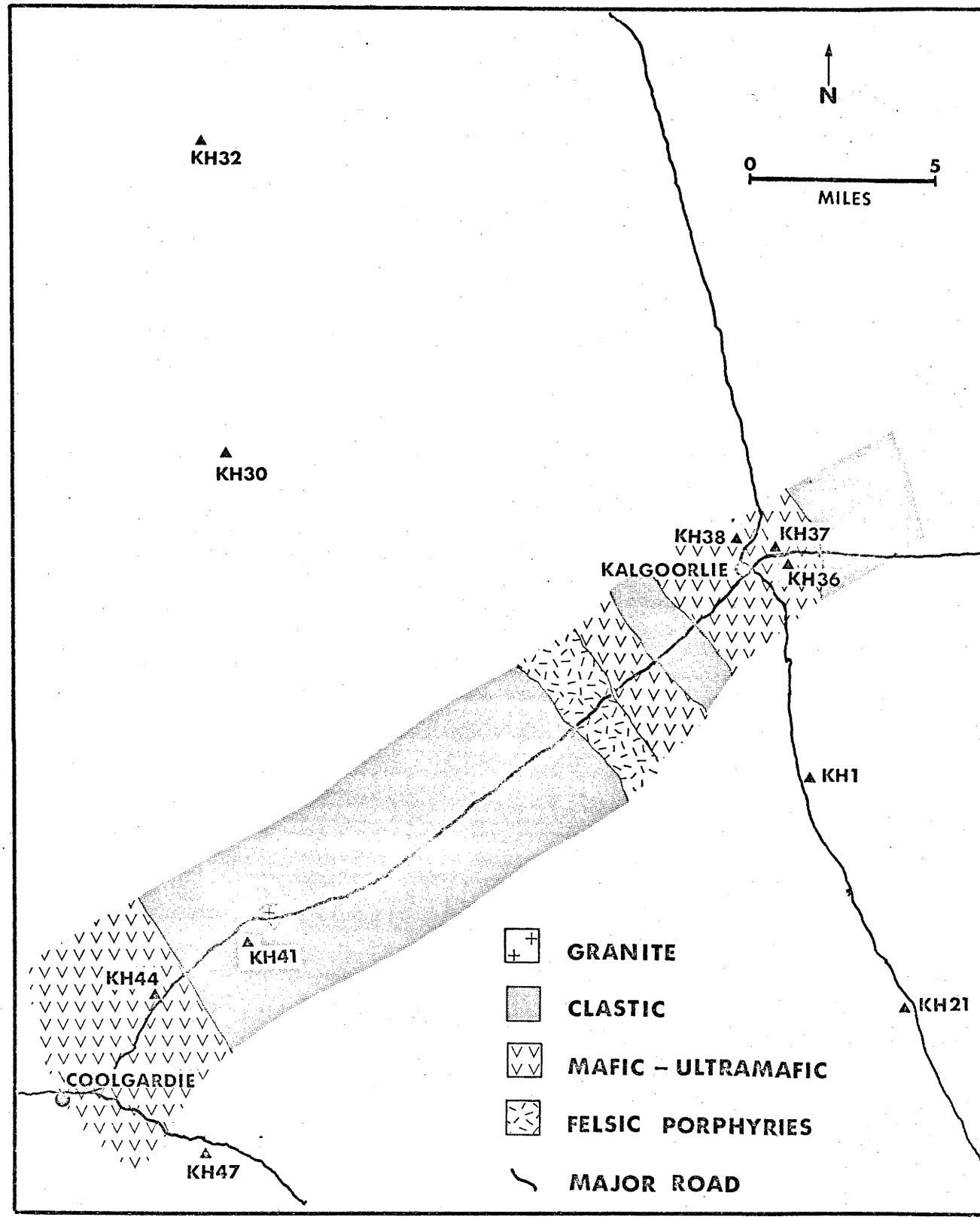

Fig. 5.7 Map of the Kalgoorlie-Coolgardie area, W.A. showing sampling locations, and the geology of a section across the Kurrawang Syncline from Glikson (1971a).

The rare earth patterns of the latter samples are consistent with a mixture of roughly equal parts mafic (tholeiitic) and felsic material (see Figs. 5.5 and 5.6). The close proximity of these sediments to the mafic rocks strongly supports this interpretation of their provenance. As discussed previously, the rare earth pattern of KH41 is possibly the result of weathering and depositional effects, and so it is not considered.

The close similarity of rare earth patterns of samples from the Coolgardie Belt (average LREE/ HREE = 6.5) to those in the Kalgoorlie Belt (average ΣLREE/ΣHREE = 6.3) is worthy of note. Insofar as the sedimentary rare earth patterns reflect the upper crustal composition at the time of deposition, the relative abundance of the different types of rocks exposed to weathering in the Kalgoorlie and Coolgardie Belts appears to have been about the same. This may have some significance in relation to the relative stratigraphic level and age of the two belts.

Archaean crustal development in the Kalgoorlie area

The rare earth data for Archaean sediments of the Kalgoorlie region have some important implications for crustal development in the area. The rare earth data suggests that a bimodal distribution of tholeiitic and felsic rocks existed during deposition of the clastic sequence. Ultramafic rocks, which were also present, are probably related to the more abundant tholeiitic suite, since both are believed to represent partial melts of the upper mantle (Nicholls and Ringwood, 1973; D. Green, 1972, 1975; Kay et al. 1970).
Detritus from the ultramafic rocks would only have a small effect on the sedimentary rare earth patterns, because of the very low abundances of rare earths in these rocks.

Recent work in experimental petrology has shown that it is very unlikely the felsic rocks could have resulted from direct partial

melting of the upper mantle (Nicholls and Ringwood, 1973; D. Green and Ringwood, 1969; Nicholls, 1974). The very low initial $^{87}Sr/^{86}Sr$ ratios of these rocks are not consistent with a felsic or sedimentary parent, but are consistent with a tholeiitic parent (Compston and Turek, 1973; Roddick, 1974). The low ΣREE in the Kambalda Granite is also not consistent with derivation by partial melting of felsic igneous or sedimentary rocks, since the melt would normally be enriched in the light rare earths relative to the parent rock. If the felsic rocks are assumed to have been derived from partial melting of tholeiites with rare earth abundances equal to the hypothetical tholeiite used in Figs. 5.5 and 5.6, then the abundances of light rare earths in KH21 require that less than 10% partial melting occurred to produce the average source rocks of this sediment. The light rare earth abundances of the Kambalda granite would allow up to 20% melting of the tholeiite.

The rare earth patterns of the felsic rocks are characterized by the lack of Eu anomalies and by extreme depletions in the heaviest rare earths. These features provide evidence as to the conditions which existed in the source regions of these rocks. Plagioclase is a solidus phase in most rock compositions at pressures up to at least 10 kb (D. Green and Ringwood, 1967; T. Green and Ringwood, 1968; T. Green, 1972; T. Green and Ringwood, 1972). Because of the silicic nature of these rocks, it seems likely that melting took place under wet conditions, which depress quartz stability (T. Green and Ringwood, 1968). Wet conditions also serve to depress plagioclase stability (T. Green, 1972). Magma produced by small degrees of partial melting at pressures below about 10 kb will probably be deficient in Eu due to residual plagioclase in the source. Melting at still lower pressures will produce larger Eu anomalies due to the enhanced stability of plagioclase. Garnet does not appear to be a stable phase above the solidus (at least in tholeiitic

compositions) until pressures of about 10 kb are reached. There is considerable uncertainty about data on garnet stability at pressures below 10 kb due to nucleation problems with garnet in experimental runs (T. Green, 1972). The presence of garnet in the residual phase during partial melting will produce a depletion in the melt of the heaviest rare earths. Thus, at pressures at which garnet appears above the solidus plagioclase begins to disappear. The pressure at which this occurs depends upon the composition of the material melted, and the experimental data available does not precisely fix this point for any particular composition, although 10 kb appears to be a reasonable estimate for the tholeiitic composition. This effect should result in an inverse correlation between relative depletion of the heaviest rare earths (La/Yb) and Eu anomalies over a certain pressure range. This is possibly demonstrated by Fig. 5.8, which shows the chondrite normalized rare earth patterns of two granites with nearly identical major element composition, taken from a compilation of standard rock data by Flannagan (1973). The granite showing a larger depletion in the heaviest rare earths also shows a greatly reduced Eu anomaly.

If this approach is applied to the felsic rocks in the Kalgoorlie area, then they must be assumed to have been derived at pressures at which garnet but not plagioclase is stable above the solidus. As previously noted, this corresponds to pressures at least above 10 kb. Thus, the rare earth data suggests that these rocks were derived by partial melting of a tholeiitic parent at depths exceeding 40 km.

The island arc analogy provides a mechanism by which tholeiitic rocks can be carried down in subduction zones to the required depths. However, as previously discussed, the calc-alkaline rocks of modern island arcs do not show the extreme depletion of the heaviest rare earths

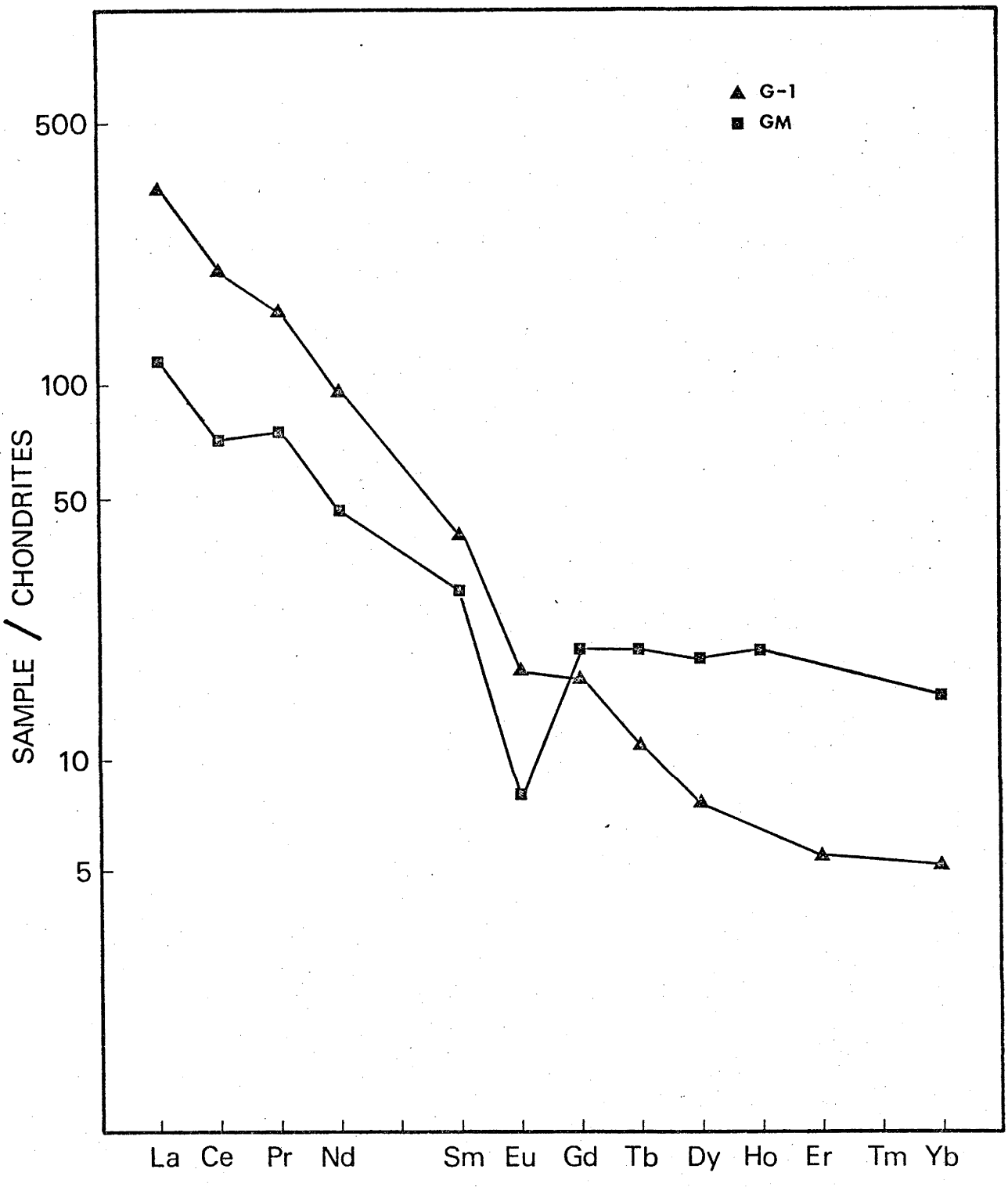

Fig. 5.8 Chondrite normalized rare earth patterns of the granite reference samples U.S.G.S.-G-1 and Z.G.I.-GM. Data is from Flanagan (1973).

characteristic of the Archaean felsic rocks. If we assume that the rare earth patterns of modern island arc calc-alkaline rocks are due to reaction of slab melts with overlying mantle or mixing with mantle derived melts, as suggested by Nicholls and Ringwood (1973), T. Green and Ringwood (1972), Nicholls (1974) and Ringwood (1974), then conditions must have been different in the Archaean if subduction was responsible for the felsic rocks. If higher geothermal gradients existed in the Archaean, then perhaps melting took place at much higher levels on the slab, thus allowing slab melts to ascend through a much thinner wedge of mantle. Melting processes in this thin wedge of mantle would soon deplete it in low melting components, preventing any further reaction with silicic melts from the slab.

Alternatively the felsic rocks could have been derived by melting at the base of a thick tholeiitic pile. In this case the melt would only be in contact with material of a similar composition to its parent rock as it ascends, and so its composition would not be greatly altered. The main problem with this hypothesis is that it requires an Archaean crust which probably exceeded present day continental crust in thickness. Several mechanisms for crustal development in the Archaean have been proposed which could explain such a thick tholeiitic crust. Williams (1973) interpreted the geology of the Kalgoorlie - Norseman region as a graben or rift structure which formed in pre-existing crustal material and allowed mantle derived melts (tholeiitic and ultramafic) to rise along the rift zone. It is similar to the "proto-oceanic rift" mechanism proposed by Windley (1973) to explain worldwide features of Archaean greenstone terrains. D. Green (1975) has suggested that a high geothermal gradient in the Archaean depressed the basalt to eclogite transition which is assumed to drive oceanic crust down into the mantle along subduction zones. As a result the oceanic crust was "scraped off" the descending lithosperic slab to form thick folds of tholeiitic

material, i.e. the greenstone belts.

The rare earth data presented here can only be applied to the area around Kalgoorlie, since some evidence suggests that other parts of the Eastern Goldfields may have developed in a different way (Williams, 1973; Oversby, 1975). Oversby (1975) found some granitic rocks in the Norseman area to show very radiogenic initial lead isotopic compositions, which suggest they were derived from much older crustal material that had undergone several cycles of reworking in the crust. Granitic plutons in the Kambalda and Kalgoorlie areas were found to have a more primitive initial lead isotopic composition. If the conclusions of Oversby are correct, then the Norseman granites should show rare earth patterns with negative Eu anomalies, in accordance with their presumed shallow crustal origin. Roddick (1974) considered the overall isotopic data in the Kalgoorlie, Kambalda, and Norseman areas to be consistent with the rifting model of Williams (1973).

Some granitic plutons in the Eastern Goldfields show high initial $^{87}Sr/^{86}Sr$ ratios (Arriens, 1971), which Glikson (1972) believes to be due to anatexis of older sodic granites. Direct partial melting of felsic rocks with large relative depletions of the heaviest rare earths would probably result in melts which are also depleted in the heaviest rare earths, even at shallow crustal levels. However, melting at shallow levels would probably impart a negative Eu anomaly to the melt due to the existence of large amounts of plagioclase in the residual phase. Burial and subsequent partial melting of sediments which are mixtures of felsic and tholeiitic material (as are most of the sediments analyzed here) could result in granites which do not show large relative depletions in the heaviest rare earths. Felsic rocks of the latter two types do not appear to have been an important part of the crust in the Kalgoorlie area at the times of deposition of the analyzed sediments, since no trace of a component with a negative Eu anomaly is present in the sediments. Rocks

of these types could possibly be identified in other parts of the Eastern Goldfields by determining rare earth distributions in rocks for which high initial $^{87}Sr/^{86}Sr$ ratios have been reported.

The island arc analogy has the advantage of providing a mechanism for production of both the tholeiitic and felsic rocks in the Kalgoorlie area. However, if the island arc analogy is to be applied to the Archaean, the mechanism should be modified to account for the difference in rare earth distribution between Archaean felsic to intermediate rocks and the calc-alkaline rocks of modern island arcs. Detailed geochemical comparisons between Archaean tholeiites and the tholeiites of modern island arcs do not uniquely support the island arc analogy, since a considerable amount of evidence exists which suggests that the low-K tholeiites of modern island arcs can be produced simply by hydrous partial melting of the upper mantle (Nicholls and Ringwood, 1973; Nicholls, 1974). Early degassing of the earth could have resulted in a higher water content in the Archaean upper mantle. Derivation of the felsic rocks from partial melting at the base of a thick tholeiitic pile can explain the characteristics of rare earth patterns of these rocks, but the problem of exactly how such a thick tholeiitic crust could have accumulated remains. The available data does not allow a clear choice to be made between the two mechanisms.

Post-Archaean sediments

Introduction

The overall rare earth distribution in the upper continental crust is widely assumed to be similar to that of clastic sediments (Taylor, 1964; Haskin et al., 1966; Jakeš and Taylor, 1974). This assumption is based on the proposition that the rare earth distribution shown by the NASC is characteristic of almost all Phanerozoic clastic sediments. The sediments analyzed in this study provide a means of measuring how far back in time this characteristic rare earth pattern existed. In the preceding discussion it was concluded that the Archaean sediments studied here did not necessarily differ from this characteristic pattern simply because they were Archaean. The more important factor was that they were deposited in an active orogenic zone and could thus be equated in some respects to sediments of younger orogenic zones such as the Devonian greywackes of the Baldwin Formation. The post-Archaean sediments closely resemble the NASC with respect to rare earth distribution, and may provide a valid measurement of overall upper crustal rare earth distribution through time. The small degree of variation in relative rare earth distributions which the post-Archaean sediments show is strong evidence that this characteristic sedimentary pattern does indeed represent the overall upper crust.

In the following discussions the average upper crustal abundances of the rare earths and some other trace elements are estimated from the data presented in chapter four, and are compared with some previous estimates of the upper crustal abundances of these elements. The implications of the sedimentary rare earth data for theories on the growth and evolution of continents are also discussed. The sedimentary rare earth pattern also has some important implications concerning the origin of tektites, and the chapter is concluded with a discussion of that topic.

The upper crustal rare earth pattern

The relative rare earth distributions of the post-Archaean sediments (excluding the Baldwin greywackes for reasons already discussed) show very little variation, although these samples range in age from Mesozoic to Middle Proterozoic. Table 5.3 summarizes the rare earth data for sediments from each of the five areas sampled. The values of Eu/Eu* and ΣLREE/ΣHREE are almost constant, suggesting that the overall composition of the upper crust has remained unchanged over the past 1500 million years. Fig. 5.9 shows the average chondrite normalized rare earth pattern of the post Archaean sediments compared to that of the NASC. The similarity of these two patterns is remarkable and further demonstrates the small degree of variation in rare earth distribution shown by clastic sediments derived from weathering of large areas of continental crust.

The average abundances of the rare earths and some other trace elements in the post Archaean sediments are listed in Table 5.4 along with some previous estimates of the abundances of these elements in the upper continental crust. The data for post Archaean sediments is in general agreement with the other estimates of upper crustal abundances with the exception of Cs for which the sediment value is much higher. Recent data on standard rocks shows that the Cs value for the post Archaean sediments is in accord with Cs abundances in other clastic sediments, and that the Cs abundances in igneous rocks are extremely variable (Randle, 1974). Thus, the previous estimates of Cs abundances may be too low due to the igneous rock data chosen in making the estimate, or the sediment data may be too high due to an accumulation of Cs through some process in the sedimentary cycle.

Absolute abundances

As can be seen from Table 5.3 the absolute abundances of the

Table 5.3 Summary of rare earth data for the post-Archaean sediments

Locality	Age (m.y.)	Average ΣLREE/ΣHREE	Average Eu/Eu*	Average ΣREE
Mt. Isa Group	1500	10.1±1.9	0.65±0.06	143±23
Amadeus Basin	850	9.5±1.8	0.67±0.03	140±23
State Circle Shale	440	10.2±1.7	0.69±0.05	185±21
Canning Basin	250-400	10.0±2.6	0.66±0.01	205±47
Perth Basin	200-250	9.0±1.4	0.69±0.07	200±48
All post-Archaean sediments		9.7±1.8	0.67±0.05	171±41

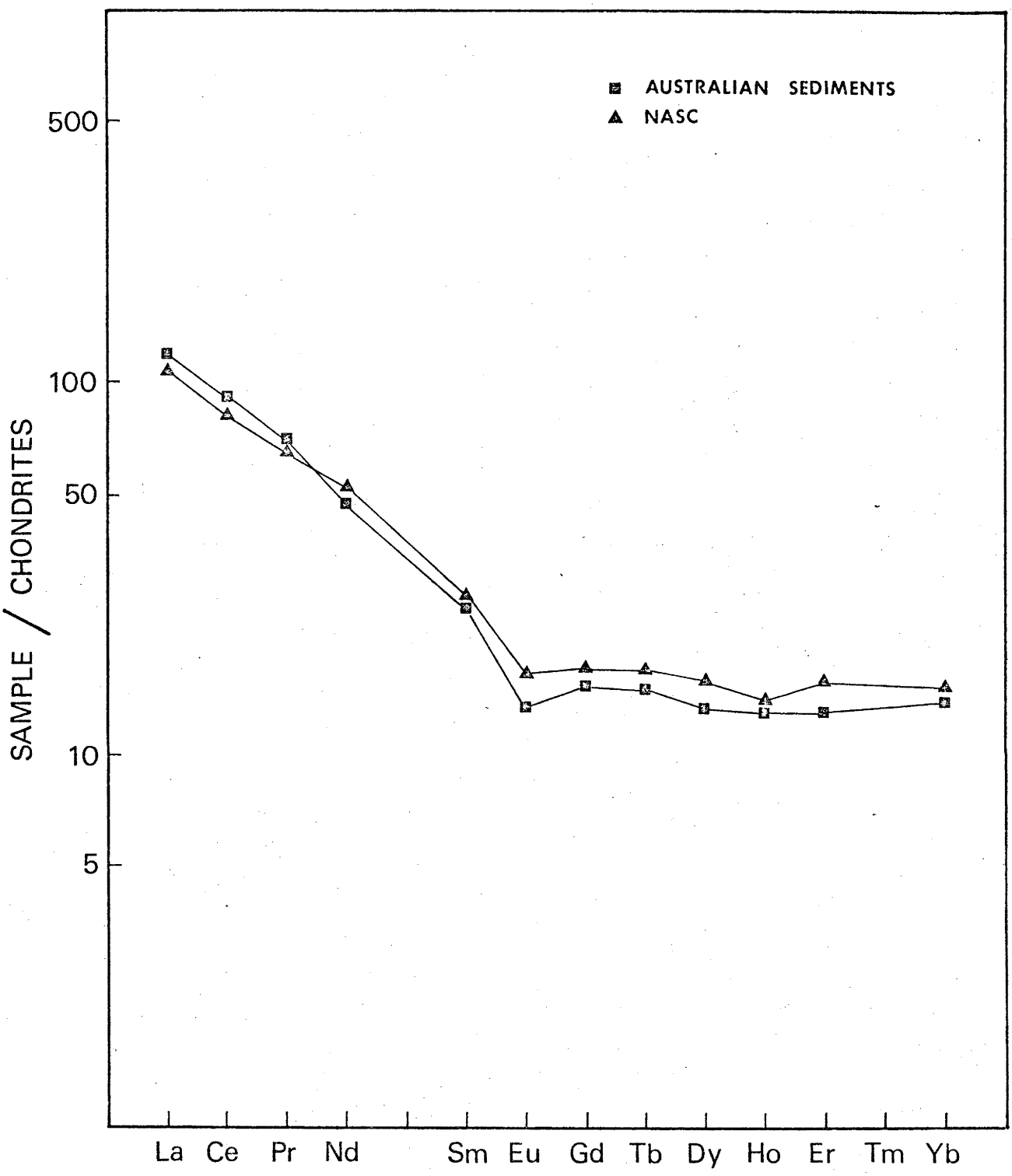

Fig. 5.9 Average chondrite normalized rare earth patterns of the post-Archaean sediments compared to that of the NASC. Data for the NASC is from Haskin et al. (1968).

Table 5.4 Average abundances of some trace elements in the post-Archaean sediments and some previous estimates of their abundances in the upper crust.

Elements	Australian sediments	NASC	Taylor, 1964	Wedepohl, 1971
Th	14		9.6	11
U	2.9		2.7	3.5
Hf	4.8		3	3
Ba	390		425	590
Cs	12		3	2.7
La	36	32	30	44
Ce	77	70	60	75
Pr	8.4	7.9	8.2	7.6
Nd	27	31	28	30
Sm	5.3	5.7	6.0	6.6
Eu	1.0	1.24	1.2	1.4
Gd	4.6	5.2	5.4	8.8
Tb	0.74	0.85	0.9	1.4
Dy	4.2	5.0	3.0	6.1
Ho	0.96	1.04	1.2	1.8
Er	2.8	3.4	2.8	3.4
Tm	0.45*		0.48	0.6
Yb	2.8	3.1	3.0	3.4
Lu	0.43*		0.50	0.6
Y	26	27	33	34

* estimates based on adjacent rare earths

rare earths (ΣREE) show a much greater degree of variation than the relative distributions. Interpretation of absolute abundances must be made with caution because of their sensitivity to the mineralogical and bulk chemical composition of the samples (Ronov et al., 1967). The data in Table 5.3 show a trend of decreasing ΣREE with increasing sediment age, but shales, subgreywackes, and siltstones are represented in the data which may tend to reflect differences in the relative number of the various rock types. If the shales alone are considered a clear trend in ΣREE with age is still evident. This trend is shown in Fig. 5.10; a plot of ΣREE vs. depositional age. With the present data it is not possible to evaluate the significance of this trend. It may simply reflect a bias in sample selection. However, it should be noted that in each case where the bulk major element chemistry of a Precambrian shale is about the same as that of a Phanerozoic shale, the younger rock has by far the higher ΣREE (e.g. A07 and PL6; PW4, PW5 and A012; MI5 and SC3) (see Tables 2.1 - 2.7 and 4.2 - 4.8). The same is true for the subgreywackes (e.g. A04 and PW9). Even so the trend cannot be considered as significant without additional data, because of the large variations in ΣREE shown by the samples. That is not to say that Fig. 5.10 does not show a definite trend, but only that the number of samples representing each age group is too small to conclude that the average represents the Australian upper crust at the time of deposition.

If the trend shown in Fig. 5.10 reflects a real upper crustal trend, then the sediment data in Table 5.4 will probably be low compared to abundances in the present day upper crust, since Precambrian samples were included in the averages. If the trend is not real, then the sediment data in Table 5.4 is probably the best estimate available for the Australian upper crust.

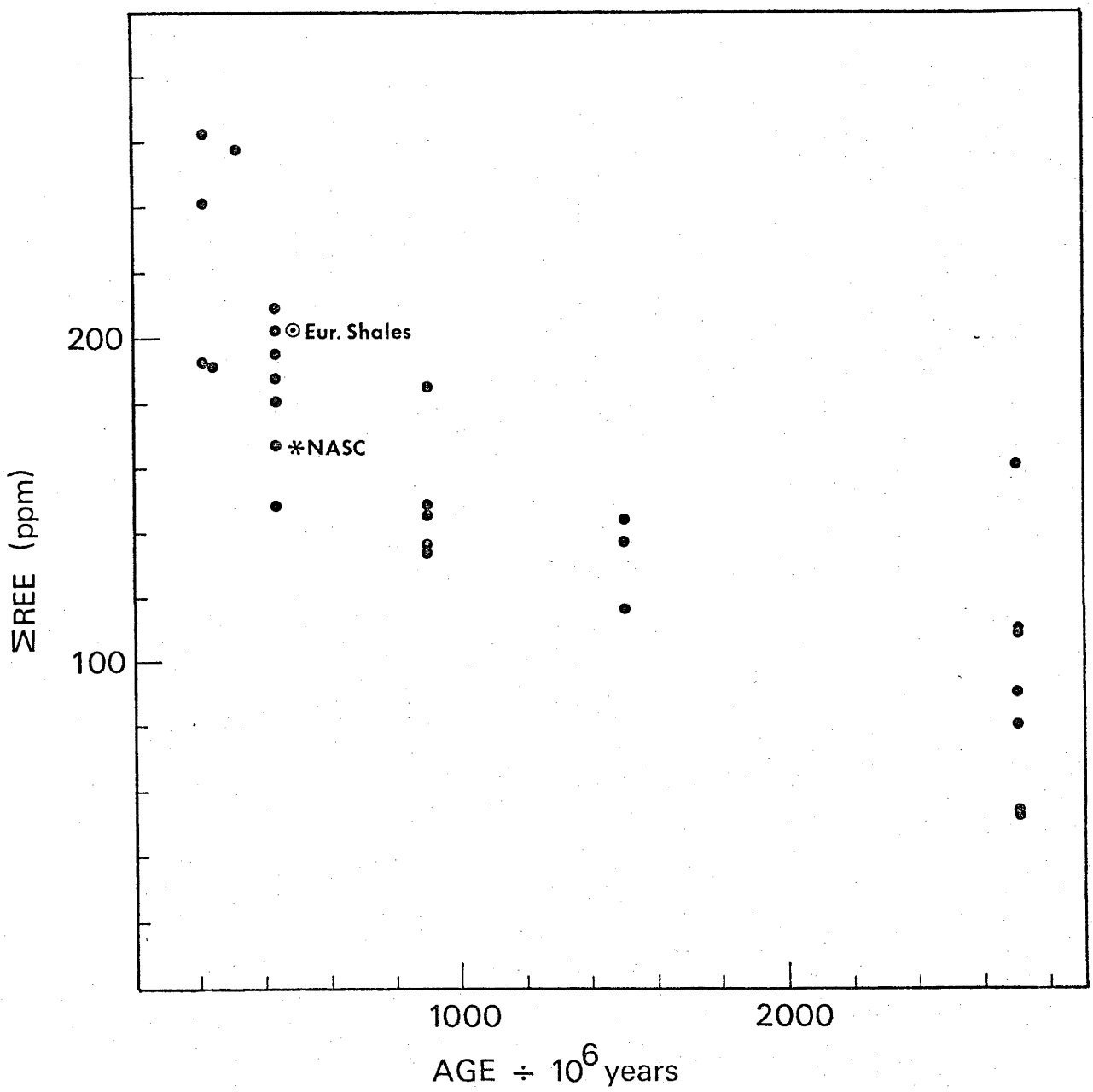

Fig. 5.10 The relationship between ΣREE and depositional age in shales. Data for the European and North American shale composites are from Haskin et al. (1968).

Theories of crustal growth and evolution

In recent years many workers have viewed island arc volcanism at continental margins as responsible for the addition of new sialic material for the growth of continents (Taylor and White, 1966; Taylor, 1967; Markhinin, 1968; Ringwood, 1969; Dickinson, 1970; Jakeš and White, 1971; D. Green, 1972; Jakeš, 1973; Jakeš and Taylor, 1974; Ringwood, 1974). This idea has been attractive to geologists because it fits into the overall theory of plate tectonics. Disparities between estimates of the chemical compositions of island arcs and the upper continental crust require that an additional chemical differentiation process operate if this theory is valid (Jakeš and White, 1971). Strong vertical stratification of the continental crust with respect to some elements has been postulated as a result of work on fractionation trends of K-Rb, Th-U, and rare earths in crustal rocks (Shaw, 1968; Lambert and Heier, 1968; Sighinolfi, 1969 and 1971; Jakeš and White, 1971; Heier, 1973). Shaw (1968) and others considered regional metamorphism to be responsible for the repeated extraction of certain elements from the lower crust throughout time, resulting in a strong vertical zonation of the crust. Jakeš and White (1972) considered partial melting in the lower crust to result in subsequent "Andean" volcanism; a process viewed as leading to a stratified crust of overall island arc composition with the upper part enriched in Si, K, Rb, Th, U, Ba and rare earths.

The model of continental growth and evolution outlined above, if correct, should result in some predictable effects upon upper crustal rare earth distribution. Jakeš and Taylor (1974) pointed out that the negative Eu anomaly in modern sediments was indicative of partial melting processes in the crust. In view of the fact that the rare earth distributions of both the upper crust and average island arc rocks can be inferred to a reasonable degree from available data, a more detailed qualitative test of this model of crustal development seems possible.

Many other models of crustal evolution have been recently discussed by various authors. The concept of a gradual evolution from a mafic to a more felsic crust has been shown to be inconsistent with the geochemical similarities between modern and ancient sediments (Condie, 1967; Schnetzler and Philpotts, 1967; Wildeman and Haskin, 1973; Wildeman and Condie, 1973). The "steady state" model of Armstrong (1968) and Armstrong and Hein (1973), which invokes continuous exchange between crust and mantle, has some features in common with the model of Jakeš and White (1971). This model does not closely define the petrogenic processes responsible for crust-mantle exchange, and so it is difficult to evaluate. Complex models such as that of Engel et al. (1974) requiring pronounced episodicity in crustal evolution are based on presumed changes in chemical composition of the crust through time. The sedimentary rare earth data is very useful in evaluating models of this type. Theories calling for the origin of continents through the infall of sialic meteorites have been proposed in recent years by Donn et al. (1965) and Van Bemmelen (1972). The latter author views crustal evolution as a gradual change from the meteoritic composition (sialic material, infalling from dust rings) to an internally derived composition. Such a model must require a continuous change in crustal composition and probably in upper crustal rare earth distribution.

Implications of the rare earth data for growth and evolution of the continental crust

The lack of variation in the relative rare earth patterns of clastic sediments over the past 1500 million years suggests that a uniformitarian system of continental growth and evolution has operated over this period. In order to make a detailed examination of the sedimentary rare earth pattern it is desirable to compare it to that of

the igneous rocks presumed to be responsible for crustal growth. A consensus has not been reached on the average composition of modern island arcs, although some estimates have been made (Jakeš and White, 1971). One possible approach to measuring the overall island arc composition would be to analyze sediments (greywackes) formed in active island arc systems, although this would not be completely satisfactory due to the apparent vertical zonation in island arc systems (Gill, 1970; Jakeš and White, 1971). Data of this type is lacking, but the greywackes of the Baldwin Formation may suit this purpose for the sake of this discussion, since they show the characteristic rare earth patterns of the low K calc-alkaline rocks of island arcs (see the discussion of Archaean sediments). These Devonian greywackes are considered to have formed from weathering debris from andesitic volcanoes on the eastern margin of Australia. Table 5.5 compares the average major element composition of the Baldwin greywackes (excluding M284 and M285 for reasons already discussed) to that of the average island arc rock of Jakeš and White (1971) and the average andesite of Taylor et al. (1969). The Ti content in the greywackes is higher than expected for island arc rocks, however it should be noted that Ti is very variable in these sediments (Table 2.5) and the high average could be due to an accumulation of Ti in the sedimentary process. Fig. 5.11 shows the average rare earth pattern of the Baldwin greywackes normalized both to chondrites and to the average post-Archaean sediment from Table 5.3. Assuming that the average rare earth pattern of the Baldwin greywackes is typical of new sialic material added to the continents, several important differences between this pattern and the observed upper crustal pattern are worthy of note.

(1) The upper crustal rare earth pattern is depleted in Eu relative to the whole crustal pattern.

(2) The upper crustal pattern is enriched in light rare earths relative to the whole crustal pattern.

Table 5.5 Average major element compositions of the Baldwin greywackes compared to the calculated average island arc composition of Jakeš and White (1971) and the average andesite of Taylor et al., (1969).

Element	Baldwin greywackes	Average island arc rock of Jakeš and White (1971)	Average andesite Taylor et al. (1969)
SiO_2	56.03	58.78	59.5
TiO_2	1.32	0.84	0.70
Al_2O_3	15.84	15.58	17.2
FeO*	10.51	7.41	6.10
MgO	4.50	4.57	3.42
CaO	5.65	8.02	7.03
Na_2O	4.69	3.39	3.68
K_2O	0.73	0.82	1.60
MnO	0.18	0.11	
P_2O_5	0.25	0.22	

* Total Fe as FeO

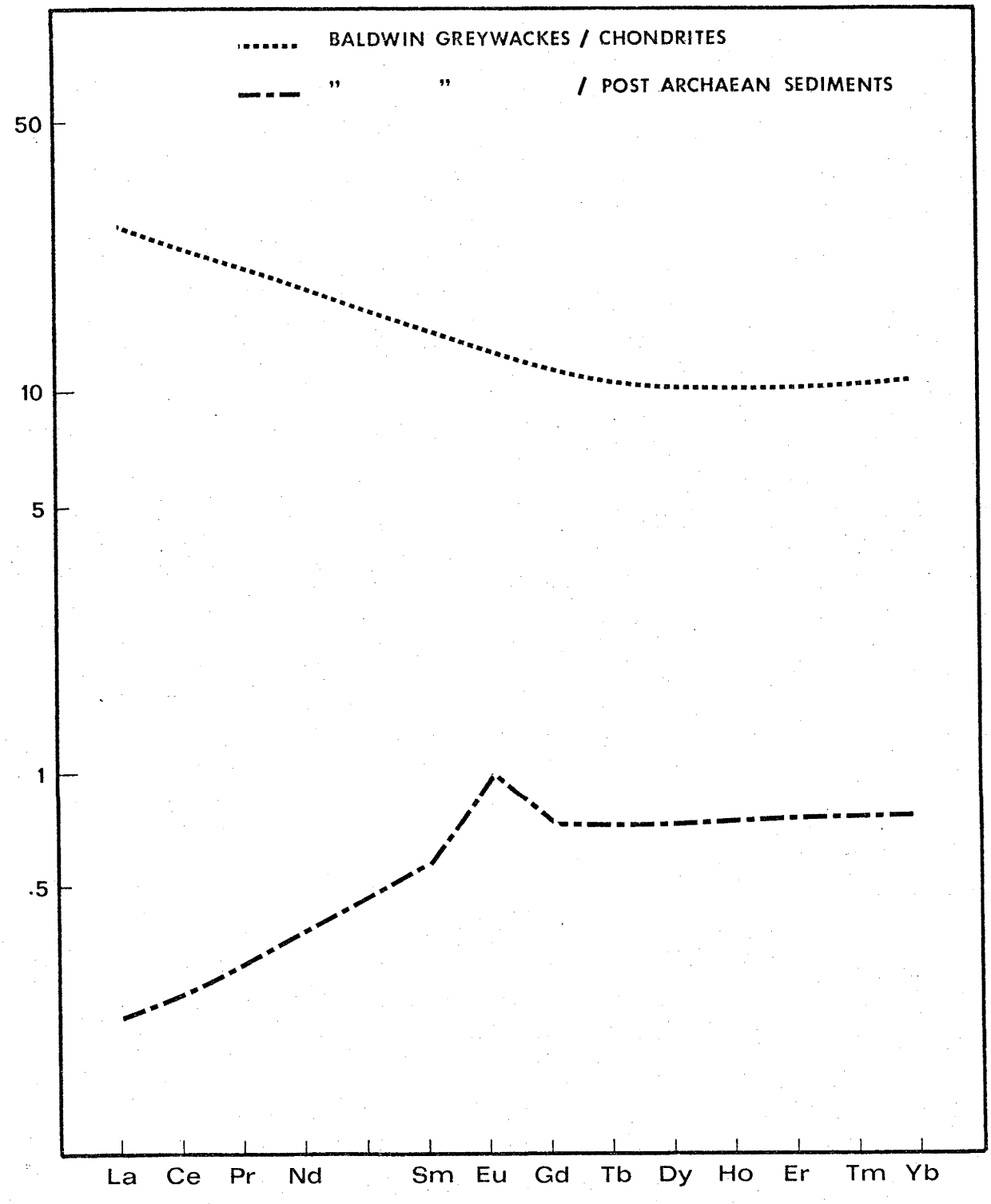

Fig. 5.11 The average rare earth abundances of the Baldwin greywackes normalized to those in chondrites and the average post-Archaean sediment.

(3) The upper crustal pattern is nearly unfractionated relative to the whole crustal pattern with respect to the heavy rare earths.

(4) The upper crust is enriched in ΣREE by a factor of about 3 relative to the whole crust.

From these differences it is clear that if the bulk crust has the composition of island arc volcanics, then an additional differentiation process is required to produce the upper crustal rare earth pattern. If this is accomplished via partial melting in the crust, some predictions can be made of the likely effects on rare earth distribution based on current knowledge in experimental petrology. Partial melting of rocks of the assumed bulk crustal composition at pressures existing throughout most of the continental crust will result in a solid residuum rich in plagioclase, clinopyroxene and possibly amphibole (T. Green and Ringwood, 1968; T. Green, 1972; Lambert and Wyllie, 1972). Some typical rare earth partition coefficients for these minerals in intermediate rocks are shown in Fig. 5.12. These partition coefficients indicate that partial melting of rocks of a similar composition to the Baldwin greywackes at crustal depths will result in a melt depleted in Eu, enriched in light rare earths and ΣREE, and nearly unfractionated in heavy rare earths relative to the parent rocks. Thus, there is good qualitative agreement between the predicted rare earth pattern of partial melts of a crust of island arc composition and the observed upper crustal rare earth pattern. A more quantitative prediction of this rare earth pattern is meaningless in view of the large variations in absolute values of rare earth partition coefficients shown by these minerals (see e.g. Nagasawa and Schnetzler, 1971).

The strong upper crustal Eu anomaly is compelling evidence of the importance of intra-crustal melting to the formation of the upper crust, since plagioclase is not a stable mean solidus phase below crustal depths (>40 km). Thus, the lower crust should show an overall enrichment

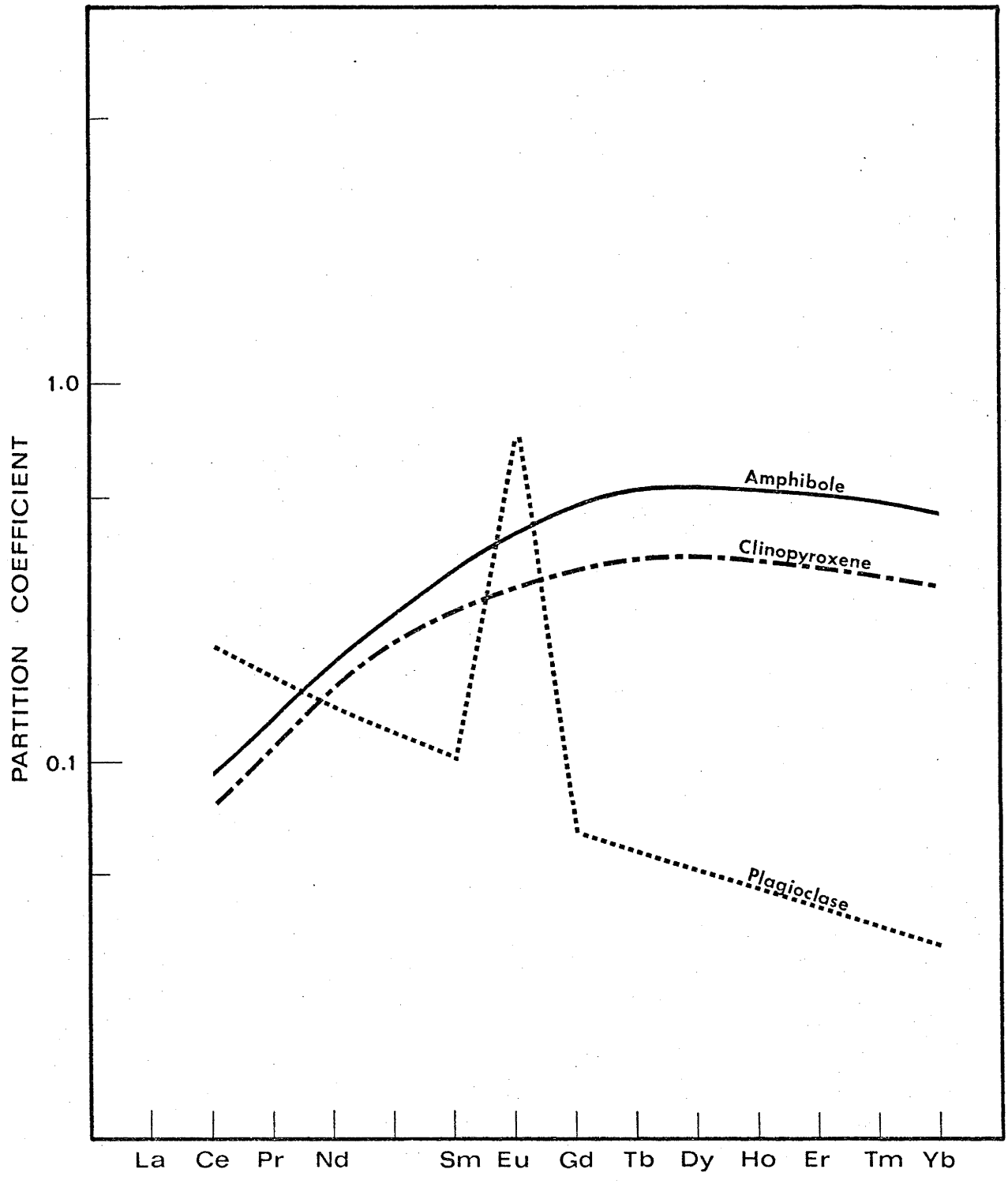

Fig. 5.12 Typical partition coefficients for the rare earths between mineral phenocrysts and matrix material in intermediate volcanic rocks. Data is from Schnetzler and Philpotts (1970).

in Eu and depletion in light rare earths and ΣREE relative to the whole crust. Although plagioclase is indicated as a major component of the lower crust, published rare earth patterns of anorthosites (T. Green et al., 1972; O'Nious and Pankhurst, 1974) reveal that most anorthosites do not show the predicted features of rare earth distribution (with the exception of positive Eu anomalies) of the overall lower crust. Nearly pure plagioclase rocks may be an important rock type in the lower crust as proposed by several workers (T. Green, 1969; Taylor, 1967; Lambert and Heier, 1968). However, an overall composition for the lower crust more enriched in pyroxene and/or amphibole than are anorthosites is indicated by the rare earth data.

The unfractionated (flat) upper crustal heavy rare earth pattern suggests that garnet is relatively unimportant as a residual phase in most crustal melting episodes. This can be clearly seen from the rare earth patterns of most granitic and granodioritic rocks, since they are usually similar to the overall upper crustal pattern (e.g. Haskin et al., 1968). Numerous experimental studies have shown that partial melting at crustal levels produces liquids of granodioritic to granitic composition as the low melting fraction (e.g. Brown and Fyfe, 1970). Those granitic rocks with large depletions in the heaviest rare earths (e.g. Arth and Hanson, 1972; Buma et al., 1971; see also Fig. 5.8 this thesis) may possibly be restricted to areas of unusually thick crust, or they may simply be melts from the deepest levels of the crust. In either case, the sedimentary rare earth data indicates that such rocks are volumetrically unimportant in the modern crust, although they appear to have been a major rock type in some Archaean terrains.

The constant nature of the upper crustal rare earth pattern over the past 1500 million years does not favour models of slow crustal evolution through repeated metamorphic episodes as suggested by Shaw (1968). It seems more likely that new crustal material rapidly evolves

to a stratified and stable form. Lewis and Spooner (1973) came to a similar conclusion from Sr isotopic studies in granulite terrains. In contrast to this, the trend in ΣREE shown in Fig. 5.10, if real, would indicate a slow evolutionary process of some kind has been operative. This process would need to increase ΣREE in the upper crust throughout time without changing the relative distribution of the rare earths. One possibility is simply an evolutionary decrease in the overall degree of partial melting, perhaps due to a cooling earth (i.e. the continuous decrease in the amount of radioactive decay). The same effect could also apply to the new sialic material added to the continents. Alternatively the trend in ΣREE could perhaps be due to a process of exchange between the lower crust and upper mantle as suggested by Shaw (1968), Armstrong (1968), Jakeš and White (1971), and Jahn et al. (1974), but it is not clear how such an exchange could lead to increased ΣREE in the upper crust. It seems more likely that exchange between the lower crust and mantle would simply result in a thickening upper crust with little or no change in the abundance of ΣREE. The model of irreversible differentiation of the earth proposed by Ringwood (1974) removes many of the reasons for postulating crust-mantle exchange. Some apparent chemical trends in the composition of sediments through time (e.g. variations in K/Na ratios) have been ascribed by some workers to sedimentary recycling processes (Garrels and Mackenzie, 1971; Veizer, 1973). Recycling processes may account for some chemical changes such as in K/Na ratios, since these elements are easily fractionated in the sedimentary cycle (i.e. K is enriched relative to Na with increasing sedimentary maturity). However, it seems doubtful that sedimentary processes alone could also result in a increase through time of the rare earth abundances in clastic sediments. It seems more probable that this trend would be due to a gradual change in abundance of ΣREE in the igneous rocks contributing to the sediments. Koljonen and Rosenberg (1974) reported

that the ΣREE abundances in young granitic rocks seem to be higher than those in their older counterparts, but their conclusion is subject to the same uncertainty of sampling validity as the trend reported here (i.e. insufficient number of samples for the large range of rock ages). Further evaluation of these possibilities is not possible without confirmation and refinement of the trend shown in Fig. 5.10.

The rare earth data does not rule out any models of continental growth and evolution which allow for crustal stratification via intra-crustal melting. However, all models are constrained by the rare earth data to account for the specific features of rare earth distribution of the whole crust (e.g. unfractionated heavy rare earths) previously discussed. The rare earth data for post-Archaean sediments strongly supports a two stage model for growth and evolution of the continental crust as proposed by Taylor (1967), Jakeš and White (1971) and Jakeš and Taylor (1974). This form of growth and evolution seems to have extended back to at least the Middle Proterozoic. The differences in rare earth distribution between the Archaean and post-Archaean sediments suggest that this model may not apply to the Archaean terrains. Alternatively, some of the differences may be due to subsequent denudation of the Archaean upper crust as proposed by Fahrig and Eade (1968). These authors suggested that erosion has removed an upper crustal layer from the Archaean terrains, thereby exposing a deeper level of crust than is normally seen in younger crustal segments. However, the low grade of metamorphism (largely greenschist) shown by the Archaean sediments severely limits the depths to which they can have once been buried. The bulk of evidence seems to indicate that the Archaean terrains did not develop in a strictly parallel way to younger crustal segments.

The sedimentary rare earth pattern and the origin of tektites

Geochemical studies on lunar rocks returned by the Apollo

missions have been damaging to the theory of a lunar origin for tektites (King et al., 1970; Schnetzler, 1970; Levinson and Taylor, 1971). The rare earth patterns of all lunar rocks examined to date are distinctly different from those of tektites (Haskin and Gehl, 1963; Taylor, 1966 and 1973; Frey et al., 1970). Tektite rare earth patterns show a general similarity to those of sediments, and many proponents of a terrestrial origin for tektites have favoured meteoritic or cometary impact on sediments and soils as the most likely mode of origin (Cherry and Taylor, 1961; Schwarcz, 1962; Taylor, 1966).

In Fig. 5.13 the chondrite normalized rare earth pattern for the post-Archaean sediments is compared to that of an australite. The similarity between these two patterns is striking, and leaves little doubt that this tektite had an origin in the upper crust. Other australites analyzed to date have the same relative rare earth pattern, and show small variations (<30%) in absolute abundances (S.R. Taylor, unpublished data). The small degree of variation in relative rare earth patterns shown by sediments (and by tektites) probably means that rare earth data is not a very promising tool for selecting specific sites for tektite origin.

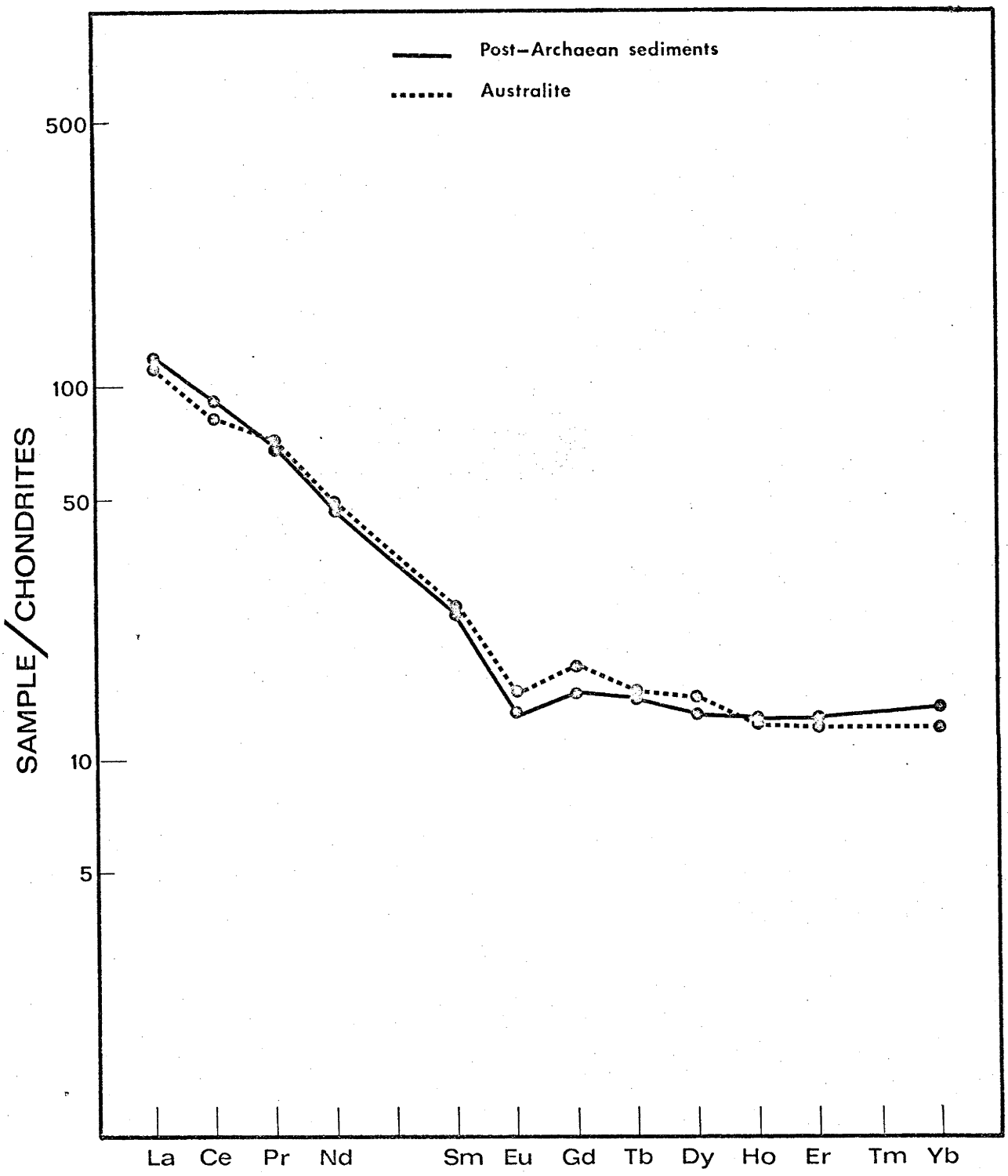

Fig. 5.13 A comparison of the chondrite normalized rare earth patterns of the average post-Archaean sediment and an australite. Rare earth data for the australite is from S.R. Taylor (pers. comm.).

Chapter 6

Conclusions

The sedimentary rare earth data presented here has provided some significant evidence regarding the development and evolution of the Australian crust. It has been assumed from the outset of this project that the study of clastic sediments would be useful in evaluating the large scale processes involved in the evolution of continents. The results have largely confirmed this assumption.

The major conclusions reached in the preceding discussions are summarized below.

(1) Clastic sediments usually show little variation in relative rare earth distribution. The "sedimentary" rare earth pattern is probably characteristic of the overall upper continental crust. However, some sediments deposited in active orogenic zones show large variations from the usual "sedimentary" rare earth pattern. These variations probably reflect the nature of igneous activity in the orogenic zone.

(2) The effects of weathering on rare earth distribution seem to be important only in zones of intense weathering such as in some types of soil profiles. Residual soils formed from weathering in a warm, humid climate show large relative depletions in the light rare earths due to acid leaching by ground water.

(3) The overall upper crustal rare earth pattern suggests that the upper crust is a product of intra-crustal melting. The composition of the upper crust is approximately granodioritic, while the composition of the whole crust is probably similar to that of average island arc volcanics. The transition from island arc type crust to chemically zoned, mature continental crust probably proceeds to completion over a relatively short period of time (less than a few hundred million years).

(4) The overall relative rare earth distribution of the upper continental crust (as shown by clastic sediments) has not changed over

the past 1500 million years. It is reasonable to assume from this that the processes responsible for crustal growth and development have remained the same over this period of time. The data suggest, but not conclusively so, that the absolute abundances of the rare earths in the upper crust have gradually increased through time. This trend could possibly be related to the decrease in heat production from radioactive decay through time. The effect of this could be to reduce the average degree of partial melting during magma genesis, resulting in higher rare earth abundances in the melt fractions. If this hypothesis is correct, then some evolutionary increase in the upper crustal abundances of other elements which are preferentially partitioned into melt fractions (e.g. Th and Rb) would be expected.

(5) The Archaean sediments of the Kalgoorlie area, Western Australia were probably derived largely from weathering of a bimodal suite of felsic and mafic volcanic-plutonic rocks. The felsic rocks are Na-rich and highly depleted in heaviest rare earths, suggesting they are the result of partial melting in the presence of garnet. In this respect they are different from the calc-alkaline rocks of modern island arcs. The apparent absence of island arc type calc-alkaline rocks in the Kalgoorlie area does not support the analogy often drawn between Archaean granite-greenstone terrains and modern island arcs. A possible explanation of the Na-rich felsic rocks is that they are the result of partial melting at the base of a thick (>40 km.) crust of tholeiitic basalt. Such a deep level origin is also consistent with the lack of negative Eu anomalies in these rocks, and thus in the sediments derived from them. The differences in rare earth distributions between Archaean and post-Archaean sediments suggest that either the Archaean crust developed by different processes to the younger crust or subsequent denudation of Archaean terrains has exposed deep crustal levels not usually seen in younger terrains.

(6) Australites show rare earth distributions very similar to that of the average clastic sediment. This suggests that these tektites had an origin in the upper crust, possibly from meteoritic or cometary impact upon sedimentary rocks.

References

Anhaeusser C.R. (1971a) The Barberton Mountain Land, South Africa - a guide to the understanding of the Archaean geology of Western Australia. Spec. Publ. Geol. Soc. Aust. 3, 103-119.

Anhaeusser C.R. (1971b) Cyclic volcanicity and sedimentation in the evolutionary development of Archaean greenstone belts of shield areas. Spec. Publ. Geol. Soc. Aust. 3, 57-70.

Anhaeusser C.R. (1973) The evolution of the Early Precambrian crust of Southern Africa. Phil. Trans. Roy. Soc. London (A) 273, 359-388.

Armstrong R.L. (1968) A model for the evolution of strontium and lead isotopes in a dynamic earth. Rev. Geophys. 6, 175-199.

Armstrong R.L. and Hein, S.M. (1973) Computer simulation of Pb and Sr isotope evolution of the earth's crust and upper mantle. Geochim. Cosmochim. Acta 37, 1-18.

Arriens P.A. (1971) The Archaean geochronology of Australia. Spec. Publ. Geol. Soc. Aust. 3, 11-23.

Arth J.G. and Hanson G.N. (1972) Quartz diorites derived by partial melting of eclogite or amphibolite at mantle depths. Contrib. Mineral. Petrol. 37, 161-174.

Balashov Yu. A. and Goryainov P.M. (1966) Rare earth elements in the Precambrian iron-bearing rocks of the Imandra region. Geochem. Int. 3, 240-251.

Balashov Yu. A., Ronov A.B., Migdisov A.A. and Turanskaya N.V. (1964) The effect of climate and facies environment on the fractionation of the rare earths during sedimentation. Geochemistry 10, 951-969.

Baragar W.R.A. (1966) Geochemistry of the yellowknife volcanic rocks. Can. J. Earth Sci. 3, 9-30.

Baragar W.R.A. and Goodwin A.M. (1969) Andesites and Archaean volcanism of the Canadian shield. Oregon Dept. Geol. Miner. Industries Bull. 65, 121-142.

Bennett E.M. (1965) Lead-zinc-silver and copper deposits of Mount Isa. In Geology of Australian Ore Deposits, (editor J. McAndrew), pp. 233-246. 8th Comm. Min. Metall. Congr., Melbourne.

Bofinger V.M., Compston W. and Gulson B.L. (1970) A Rb-Sr study of the Lower Silurian Stage (sic) Circle Shale, Canberra Australia. Geochim. Cosmochim. Acta 34, 433-445.

Bridgewater D., Watson J. and Windley B.F. (1973) The Archaean craton of the North Atlantic region. Phil. Trans. Roy. Soc. London (A) 273, 493-512.

Brown D.A., Cambell K.S.W. and Crook K.A.W. (1968) The geological evolution of Australia and New Zealand. Pergamon.

Brown G.C. and Fyfe W.S. (1970) The production of granitic melts during ultrametamorphism. Contrib. Mineral. Petrol. 28, 310-318.

Buma G., Frey F.A. and Wones D.R. (1971) New England Granites: Trace element evidence regarding their origin and differentiation. Contrib. Mineral. Petrol. 31, 300-320.

Chappell B.W. (1968) Volcanic greywackes from the Upper Devonian Baldwin Formation, Tamworth-Barraba District, New South Wales. J. Geol. Soc. Aust. 15, 87-102.

Cherry R.D. and Taylor S.R. (1961) Studies of tektite compositions - II Derivation from a quartz-shale mixture. Geochim. Cosmochim. Acta 22, 164-168.

Compston W. and Arriens P.A. (1968) The Precambrian geochronology of Australia. Can. J. Earth Sci. 5, 561-583.

Compston W. and Turek A. (1973) Isotopic age limits for the provenance and deposition of the Kurrawang Beds, Coolgardie Goldfield, Western Australia. J. Geol. Soc. Aust. 20, 217-222.

Condie K.C. (1967) Geochemistry of Early Precambrian greywackes from Wyoming. Geochim. Cosmochim. Acta 31, 2135-2149.

Condie K.C. and Baragar W.R.A. (1974) Rare-earth element distribution in volcanic rocks from Archaean greenstone belts. Contrib. Mineral. Petrol. 45, 237-246.

Condon M.A. (1968) The Geology of the Carnarvon Basin, Western Australia. Bur. Min. Resour. Aust. Bull. 77.

Coryell C.D., Chase J.W. and Winchester J.W. (1963) A procedure for geochemical interpretation of terrestrial rare-earth abundance patterns. J. Geophys. Res. 68, 559-566.

Cullers R.L., Mendaris L.G. and Haskin L.A. (1973) Experimental studies of the distribution of rare earths as trace elements among silicate minerals and liquids and water. Geochim. Cosmochim. Acta 37, 1499-1512.

Cullers R.L., Yeh L.T., Chauduri S. and Guidotti C.V. (1974) Rare-earth elements in Silurian pelitic schists from N.W. Maine. Geochim. Cosmochim. Acta 38, 389-400.

Dickinson W.R. (1970) Relations of andesites, granites and derivative sandstones to arc-trench tectonics. Rev. Geophys. Space Sci. 8, 813-860.

Donn W.L., Donn B.D. and Valentine W.G. (1965) On the early history of the earth. Bull. Geol. Soc. Amer. 76, 287-306.

Dunn P.R., Plumb K.A. and Roberts H.G. (1966) A proposal for time-stratigraphic subdivision of the Australian Precambrian. J. Geol. Soc. Aust. 13, 593-608.

Engel A.E.J. (1963) Geologic evolution of North America. Science 140, 143-152.

Engel A.E.J., Itson S.P., Engel C.G., Stickney D.M. and Cray E.J. (1974) Crustal evolution and global tectonics: a petrogenic view. Bull. Geol. Soc. Amer. 85, 843-858.

Fahrig W.F. and Eade K.E. (1968) The chemical evolution of the Canadian shield. Can. J. Earth Sci. 5, 1247-1252.

Flanagan F.J. (1973) 1972 values for international geochemical reference samples. Geochim. Cosmochim. Acta 37, 1189-1200.

Folinsbee R.E., Baadsgaard H., Cumming G.L. and Green D.C. (1968) A very ancient island arc. Amer. Geophys. Union. Monogr. 12, 441-448.

Frey F.A., Spooner C.M. and Baedecker P.A. (1970) Microtektites and tektites: A chemical comparison. Science 170, 845-847.

Gardner W.E. (1963) Well completion report, Langoora No. 1. West. Aust. Petroleum Pty. Ltd.

Garrels R.M. and Mackenzie F.T. (1971) Evolution of Sedimentary Rocks. Norton.

Gavrilova L.K. and Turanskaya R.V. (1958) Distribution of rare-earths in rock-forming and accessory minerals of certain granites. Geochemistry 2, 163-170.

Gélinas L. and Brooks C. (1973) Archaean quench-texture tholeiites. Can. J. Earth Sci. 11, 324-340.

Gill J.B. (1970) Geochemistry of Viti Levu, Fiji, and its evolution as an island arc. Contrib. Mineral. Petrol. 27, 179-203.

Glikson A.Y. (1970) Geochemical evolution and geochemical affinities of Early Precambrian systems. Tectonophysics 9, 397-433.

Glikson A.Y. (1971a) Archaean geosynclinal sedimentation near Kalgoorlie, Western Australia. Spec. Publ. Geol. Soc. Aust. 3, 443-460.

Glikson A.Y. (1971b) Primitive Archaean element distribution patterns: chemical evidence and geotectonic significance. Earth Planet. Sci. Lett. 12, 309-320.

Glikson A.Y. (1972) Early Precambrian evidence of a primitive ocean crust and island nuclei of sodic granite. Bull. Geol. Soc. Amer. 83, 3323-3314.

Glikson A.Y. and Lambert I.B. (1973) Relations in space and time between major Precambrian shield units: an interpretation of Western Australian data. Earth Planet. Sci. Lett. 20, 395-403.

Glikson A.Y. and Sheraton J.W. (1972) Early Precambrian trondhjemitic suites in Western Australia and Northwestern Scotland and the geochemical evolution of shields. Earth Planet. Sci. Lett. 17, 227-242.

Goldschmidt V.M. (1937) The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc., 655-673.

Goldschmidt (1938) Geochemische Verteilungsgesetze der Elemente IX. Die Mengenverhaltnisse der Elemente und Atom-Arten. Norske Videnskaps-Akad. Skr. M.N. Kl. 4, 1-148.

Goles G.G. (1968) Rare-earth geochemistry of Precambrian plutonic rocks. 23 Int. Geol. Conf. 6, 237-249. Prague.

Goodwin A.M. (1973) Plate tectonics and evolution of Precambrian crust. In Implications of Continental Drift to the Earth Sciences, (editors D.H. Tarling and S.K. Runcorn), Vol. 2, pp. 1047-1069. Academic Press.

Gordon M., Tracey J.I. and Ellis M.W. (1958) Geology of the Arkansas bauxite region. U.S. Geol. Surv. Profess. Papers 299.

Gorton M.P. (1974) The geochemistry and geochronology of the New Hebrides. Unpubl. Thesis, Aust. Nat. Univ.

Graf D.L. (1960) Geochemistry of carbonate sediments and sedimentary carbonate rocks. Part III, Minor element distribution. Illinois Geol. Survey Circ. 301, 1-71.

Green D.H. (1972) Magmatic activity as the major process in the chemical evolution of the earths crust and mantle. Tectonophysics 13, 47-71.

Green D.H. (1975) Genesis of Archaean peridotitic magmas and constraints on Archaean geothermal gradients and tectonics. Geology 3, 15-18.

Green D.H. and Ringwood A.E. (1967) An experimental investigation of the gabbro to eclogite transformation and its petrological applications. Geochim. Cosmochim. Acta 31, 767-833.

Green D.H. and Ringwood A.E. (1969) The origin of basalt magmas. Amer. Geophys. Union Monogr. 13, 489-495.

Green T.H. (1969) High-pressure experimental studies on the origin of anorthosite. Can. J. Earth Sci. 6, 427-440.

Green T.H. (1972) Crystallization of calc-alkaline andesite under controlled high-pressure hydrous conditions. Contrib. Mineral. Petrol. 34, 150-166.

Green T.H., Brunfelt A.O. and Heier K.S. (1972) Rare-earth element distribution and K/Rb ratios in granulites, mangerites and anorthosites, Loften-Vesteraalen, Norway. Geochim. Cosmochim. Acta 36, 241-257.

Green T.H. and Ringwood A.E. (1968) Genesis of the calc-alkaline igneous rock suite. Contrib. Mineral. Petrol. 18, 105-162.

Green T.H. and Ringwood A.E. (1972) Crystallization of garnet-bearing rhyodacite under high pressure hydrous conditions. J. Geol. Soc. Aust. 19, 203-212.

Hallberg J.A. (1972) Geochemistry of Archaean volcanic belts in the Eastern Goldfields region of Western Australia. J. Petrol. 13, 45-56.

Hanson G.N. and Goldich S.S. (1972) Early Precambrian rocks in the Saganaga Lake - Northern Light Lake area, Minnesota-Ontario Part II: petrogenesis. Geol. Soc. Amer. Memoir 135, 179-192.

Hart S.R., Brooks C., Krough T.W., Davis G.L. and Nava D. (1970) Ancient and modern volcanic rocks: a trace element model. Earth Planet. Sci. Lett. 10, 17-28.

Haskin M.A. and Haskin L.A. (1966) Rare earths in European shales: a redetermination. Science 154, 507-509.

Haskin L.A., Frey F.A., Schmitt R.A. and Smith R.H. (1966) Meteoritic, solar and terrestrial rare-earth distributions. Phys. Chem. Earth. 7, 169-321. Pergamon.

Haskin L. and Gehl M.A. (1962) The rare-earth distribution in sediments. J. Geophys. Res. 67, 2537-2541.

Haskin L. and Gehl M. (1963) The rare-earth distribution in tektites. Science 139, 1056-1058.

Haskin L.A., Haskin M.A., Frey F.A. and Wildeman T.R. (1968) Relative and absolute terrestrial abundances of the rare earths. In Origin and Distribution of the Elements, (editor L.H. Ahrens), pp. 889-912. Pergamon Press.

Heier K.S. (1973) Geochemistry of granulite facies rocks and problems of their origin. Phil. Trans. Roy. Soc. London (A) 273, 429-442.

Helmke P.A. and Haskin L.A. (1972) Rare earths and other trace elements in Apollo 15 samples. The Apollo 15 Lunar Samples, pp. 217-220. Lunar Science Institute, Houston.

Hubbard N.J. and Gast P.W. (1971) Chemical composition and origin of nonmare lunar basalts. Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2, Vol. 2, pp. 999-1020. M.I.T. Press.

Hunt C.B. (1972) Geology of soils, their evolution, classification and uses. W.H. Freeman and Co., San Francisco, pp. 344.

Hurley P.M., Hughes H., Faure G., Fairbarn H.W. and Pinson W.H. (1962) Radiogenic strontium-87 model of continent formation. J. Geophys. Res. 67, 5315-5334.

Jahn B., Shih C. and Murthy V.R. (1974) Trace element geochemistry of archaean volcanic rocks. Geochim. Cosmochim. Acta. 38, 611-627.

Jakeš P. (1973) Geochemistry of continental growth. In Implications of Continental Drift to the Earth Sciences (editors D.H. Tarling and S.K. Runcorn), Vol. 2, pp. 991-1001. Academic Press.

Jakeš P. and Gill J.B. (1970) Rare earth elements and the island arc tholeiitic series. Earth Planet. Sci. Lett. 9, 17-28.

Jakeš P. and Taylor S.R. (1974) Excess europium content in Precambrian sedimentary rocks and continental evolution. Geochim. Cosmochim. Acta 38, 739-745.

Jakeš P. and White A.J.R. (1971) Composition of island arcs and continental growth. Earth Planet. Sci. Lett. 12, 224-230.

Jakeš P. and White A.J.R. (1972) Major and trace element abundances in volcanic rocks of orogenic areas. Bull. Geol. Soc. Amer. 83, 29-40.

Kay R., Hubbard N.J. and Gast P.W. (1970) Chemical characteristics and origin of oceanic ridge volcanic rocks. J. Geophys. Res. 75, 1585-1613.

King E.A., Martin R. and Nance W.B. (1970) Tektite glass not in Apollo 12 sample. Science 170, 199-200.

Koljonen T. and Rosenberg R.J. (1974) Rare earth elements in granitic rocks. Lithos 7, 249-261.

Kriewaldt M.J.B. (1969) Explanatory notes on the Kalgoorlie sheet area. Bur. Min. Res. Aust. 1:250,000 geological series.

Lambert I.B. and Heier K.S. (1968) Geochemical investigations of deep-seated rocks in the Australian shield. Lithos 1, 30-53.

Lambert I.B. and Whylie P.J. (1972) Melting of gabbro (quartz eclogite) with excess water to 35 kilobars, with geological applications. J. Geol. 80, 693-708.

Lambert R. St J. (1971) The pre-Pleistocene Phanerozoic time-scale - a review. Spec. Publ. Geol. Soc. London 5, 9-31.

Levinson A.A. and Taylor S.R. (1971) Moon Rocks and Minerals. Pergamon.

Lewis J.D. and Spooner C.M. (1973) K/Rb ratios in Precambrian granulite terrances, Geochim. Cosmochim. Acta 37, 1111-1118.

LSPET (1972) Preliminary examination of lunar samples. Apollo 15 Preliminary Science Report, NASA SP-289, Washington.

Markhinin E.K. (1968) Volcanism as an agent of formation of the earth's crust. Amer. Geophys. Union Monogr. 12, 413-422.

Masuda A. (1962) Regularities in variation of relative abundances of lanthanide elements and an attempt to analyse separation index patterns of some minerals. J. Earth Sci., Nagoya Univ. 10, 173-187.

McGregor V.R. (1973) The Early Precambrian gneisses of the Godthåb district, West Greenland. Phil. Trans. Roy. Soc. London (A) 273, 343-358.

Minami E. (1935) Gehalte an seltenen Erden in europäischen and japenischen Tonschiefern. Nach. Gellschaft. Wissenschafen Gottingen. Math-phys. Kl. Fach IV N.F. 1, 155-170.

Morgan J.W., Krähenbühl V., Ganapathy R. and Anders E. (1972) Trace elements in Apollo 15 samples: Implications for meteorite influx and volatite depletion on the moon. Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 3, Vol. 2, pp. 1361-1376. M.I.T. Press.

Nagasawa H. and Schnetzler C.C. (1971) Partitioning of rare earth, alkali and alkaline earth elements between phenocrysts and acidic igneous magma. Geochim. Cosmochim. Acta 35, 953-968.

Nesbitt R.W. (1971) Skeletal crystal forms in the ultramafic rocks of the Yilgarn Block, Western Australia: evidence for an Archaean ultramafic liquid. Spec. Publ. Geol. Soc. Aust. 3, 331-347.

Nicholls I.A. (1974) Liquids in equilibrium with peridotitic mineral assemblages at high water pressures. Contrib. Mineral. Petrol. 45, 289-316.

Nicholls I.A. and Ringwood A.E. (1973) Effect of water on olivine stability in tholeiites and the production of silica-saturated magmas in the island-arc environment. J. Geol. 81, 285-300.

Noddack I. (1935) Die Haüfigkeiten der seltenen Erden in Meteoriten. Z. anorg. Allgem. Chem. 225, 337-364.

Ojakangas R.W. (1972) Archaean volcanogenic graywackes of the Vermilion District, Northeastern Minnesota. Bull. Geol. Soc. Amer. 83, 429-442.

O'Nions R.K. and Pankhurst R.J. (1974) Rare-earth element distribution in Archaean geneisses and anorthosites, Godthåb area, West Greenland. Earth Planet. Sci. Lett. 22, 328-338.

Öpik A.A. (1958) The geology of the Canberra City District. Bur. Min. Resour. Aust. Bull. 32.

Oversby V.M. (1975) Lead isotopic systematics and ages of Archaean acid intrusives in the Kalgoorlie - Norseman area, Western Australia. Geochim. Cosmochim. Acta, in press.

Page R.W. and Derrick G.M. (1973) Precambrian geochronology in the Mt. Isa-Cloncurry area, Northwest Queensland. 45 Cong. Aust. New Zeal. Assoc. Adv. Sci. (Abstracts) 3, 149-152. Perth.

Patterson C. and Tatsumoto M. (1964) The significance of lead isotopes in detrital feldspar with respect to chemical differentiation within the earth's mantle. Geochim. Cosmochim. Acta 28, 1-22.

Pettijohn F.J. (1957) Sedimentary Rocks, second edition. Harper and Brothers.

Pettijohn F.J. (1972) The Archaean of the Canadian shield: A resume. Geol. Soc. Amer. Memoir 135, 131-149.

Pettijohn F.J., Potter P.E. and Siever R. (1972) Sand and Sandstone. Springer-Verlag.

Philpotts J.A., Martin, W. and Schnetzler C.C. (1971) Geochemical aspects of some Japanese lavas. Earth Planet. Sci. Lett. 12, 89-96.

Planalp R.N. and Pemberton R.L. (1963) Well completion report, Exoil Ooraminna No. 1. Exoil (N.T.) Pty. Ltd.

Pudovskis V. (1963) Well completion report, Woolmulla No. 1. West Aust. Petroleum Pty. Ltd.

Pudovskis V. (1964) Well completion report, Learmonth No. 2. West Aust. Petroleum Pty. Ltd.

Randle K. (1974) Some trace element data and their interpretation for several new reference samples obtained by neutron activation analysis. Chem. Geol. 13, 237-256.

Rankhama K. (1971) The Proterozoic-Archaean time boundary. Spec. Publ. Geol. Soc. Aust. 3 (Abstract), 71.

Ringwood A.E. (1969) Composition and evolution of the upper mantle. Amer. Geophys. Union Monogr. 13, 1-17.

Ringwood A.E. (1974) The petrological evolution of island arc systems. J. Geol. Soc. 130, 183-204.

Roaldset E. (1973) Rare earth elements in Quarternary clays of the Numedal area, Southern Norway. Lithos 6, 349-372.

Robinson P.T. and Whitford D.J. (1974) Basalts from the Eastern Indian Ocean, DSDP Leg 27. In Initial Reports of the Deep Sea Drilling Project, Vol. 27, pp. 551-559, Washington (U.S. Government Printing Office).

Roddick J.C.M. (1974) Responses of Strontium Isotopes to Some Crustal Processes. Unpubl. Thesis, Aust. Nat. Univ.

Ronov A.B. (1972) Composition evolution in rocks and geochemical processes in the sedimentary shell of the earth. Geochem. Int. 9, 85-94.

Ronov A.B., Balashov Yu. A., Girin Yu. P., Bratishko R. Kh. and Kazakov G.A. (1972) Trends in rare earth distribution in the sedimentary shell and in the earth's crust. Geochem. Int. 9, 987-1016.

Ronov A.B., Balashov Yu. A. and Migdisov A.A. (1967) Geochemistry of the rare earths in the sedimentary cycle. Geochem. Int. 4, 1-17.

Ronov A.B. and Migdisov A.A. (1970) Evolution of the chemical composition of the rocks in the shields and sediment cover of the Russian and North American platforms. Geochem. Int. 7, 294-325.

Sahama Th. G. (1945) Spurenelemente der Gesteine im Südlchen Finnisch-Lappland. Bull. Comm. Geol. Finlande, 135, 1-86.

Schmitt R.A., Mosen A.W., Suffredini C.S., Lasch J.E., Sharp R.A. and Olehy D.A. (1960) Abundances of the rare-earth elements, lanthanum to lutetium, in chondritic meteorites. Nature 186, 863-866.

Schnetzler C.C. (1970) The lunar origin of tektites R.I.P. Meteoritics 5, 221.

Schnetzler C.C. and Philpotts J.A.(1967) Has the earth's crust changed with time? Rare-earth abundances in ancient sediments. Goddard Space Flight Center Report X-641-67-237, Greenbelt Md.

Schnetzler C.C. and Philpotts J.A. (1970) Partition coefficients of rare earth elements between igneous matrix material and rock forming mineral phenocrysts. II. Geochim. Cosmochim. Acta 34, 331-340.

Schubert G. and Anderson O. (1974) The earths thermal gradient. Physics Today 27, 28-33.

Schwarcz H.P. (1962) A possible origin of tektites by soil fushion at impact sites. Nature 194, 8-10.

Shaw D.M. (1968) A review of K-Rb fractionation trends by covariance analysis. Geochim. Cosmochim. Acta 32, 573-602.

Sighinolfi G.P. (1969) K-Rb ratio in high grade metamorphism. A confirmation of the hypothesis of a continual crustal evolution. Contrib. Mineral. Petrol. 21, 346-356.

Sighinolfi G.P. (1971) Investigations into deep crustal levels: Fractionating effects and geochemical trends related to high-grade metamorphism. Geochim. Cosmochim. Acta 35, 1005-1021.

Silver L.T. (1972) Uranium-thorium-lead isotopes and the nature of the mare surface debris at Hadley-Apennine. In The Apollo 15 Lunar Samples, pp. 388-390. The Lunar Science Institute, Houston.

Smith S.E. and Walker K.R. (1971) Primary element dispersions associated with mineralization at Mount Isa, Queensland. Bur. Min. Resour. Aust. Bull. 131.

Stern C.R. and Wyllie P.J. (1973) Melting relations of basalt-andesite-rhyolite-H_2O and a pelagic red clay at 30 kb. Contrib. Mineral. Petrol. 42, 313-323.

Sutton J. (1973) Some changes in continental structure since Early Precambrian time. In Implications of Continental Drift to the Earth Sciences, (editors D.H. Tarling and S.K. Runcorn), Vol. 2, pp. 1071-1081. Academic Press.

Taylor S.R. (1960) The abundance of the rare earth elements in relation to their origin. Geochim. Cosmochim. Acta 19, 100-112.

Taylor S.R. (1962) Meteoritic and terrestrial rare earth abundance patterns. Geochim. Cosmochim. Acta 26, 81-88.

Taylor S.R. (1964) Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28, 1273-1285.

Taylor S.R. (1965) Geochemical analysis by spark source mass spectrography. Geochim. Cosmochim. Acta 29, 1243-1261.

Taylor S.R. (1966) Australites, Henbury impact glass and subgreywacke: a comparison of the abundances of 51 elements. Geochim. Cosmochim. Acta 30, 1121-1136.

Taylor S.R. (1967) The origin and growth of continents. Tectonophysics 4, 17-34.

Taylor S.R. (1971) Geochemical application of spark source mass spectrography - II. Photoplate data processing. Geochim. Cosmochim. Acta 35, 1187-1196.

Taylor S.R. (1973) Tektites: A post-Apollo view. Earth Sci. Rev. 9, 101-123.

Taylor S.R., Capp A.C., Graham A.L. and Blake D.H. (1969) Trace element abundances in andesites II. Saipan, Bougainville and Fiji. Contrib. Mineral. Petrol. 23, 1-26.

Taylor S.R., Gorton M.P., Muir P., Nance W.B., Rudowski R., and Ware, N. (1973) Composition of the Descartes region, lunar highlands. Geochim. Cosmochim. Acta 37, 2665-2683.

Taylor S.R. and White A.J.R. (1966) Trace element abundances in anesites. Bull. Volcanol. 29, 174-194.

Templeton D.H. and Dauben C.H. (1954) Lattice parameters of some rare earth compounds and a set of crystal radii. J. Amer. Chem. Soc. 76, 5237-5239.

Towell D.G., Winchester J.W. and Spirn R.V. (1965) Rare-earth distributions in some rocks and associated minerals of the batholith of Southern California. J. Geophys. Res. 70, 3485-3496.

Travis G.A., Woodall R. and Bartram G.D. (1971) The geology of the Kalgoorlie goldfield. Spec. Publ. Geol. Soc. Aust. 3, 175-190.

Valeton I. (1972) Bauxites. Elsevier.

Van Bemmelen R.W. (1972) Geodynamic Models. Elsevier.

Veizer J. (1973) Sedimentation in geologic history: recycling vs. evolution or recycling with evolution. Contrib. Mineral. Petrol. 38, 261-278.

Viljoen M.J. and Viljoen R.P. (1969a) The geology and geochemistry of the lower ultramafic unit of the Onverwacht Group and a proposed new class of igneous rocks. Spec. Publ. Geol. Soc. S. Africa 2, 55-86.

Viljoen R.P. and Viljoen M.J. (1969b) The relationship between mafic and ultramafic magma derived from the upper mantle and the ore deposits of the Barberton region. Spec. Publ. Geol. Soc. S. Africa 2, 221-244.

Viljeon M.J. and Viljoen R.P. (1969c) A reappraisal of granite-greenstone terrains of shield areas based on the Barberton model. Spec. Publ. Geol. Soc. S. Africa 2, 245-274.

Vinogradov A.P. and Tugarinov A.I. (1968) Geochronological scale of the Precambrian. 23 Int. Geol. Conf. 6, 205-222. Prague.

Wanke H., Palme H., Spettel B. and Teschke F. (1972) Multielement analyses and a comparison of the degree of oxidation of lunar and meteoritic matter. In The Apollo 15 Lunar Samples, pp. 265-267. Lunar Science Institute, Houston.

Wells A.T., Forman D.J., Ranford L.C. and Cook P.J. (1970) Geology of the Amadeus Basin, Central Australia. Bur. Min. Resour. Aust. Bull. 100.

White A.J.R., Jakeš P. and Christie D.M. (1971) Composition of greenstones and the hypothesis of sea-floor spreading in the Archaean. Spec. Publ. Geol. Soc. Aust. 3, 47-56.

Wildeman T.R. and Condie K.C. (1973) Rare earths in Archaean graywackes from Wyoming and from the Fig Tree Group, South Africa. Geochim. Cosmochim. Acta 37, 439-453.

Wildeman T.R. and Haskin L. (1965) Rare-earths in ocean sediments. J. Geophys. Res. 70, 2905-2910.

Wildeman T.R. and Haskin L.A. (1973) Rare earths in Precambrian sediments. Geochim. Cosmochim. Acta 37, 419-438.

Williams I.R. (1970) Explanatory notes for the Kurnalpi sheet area. Bur. Min. Res. Aust. 1:250,000 geological series.

Williams I.R. (1973) A proposed structural subdivision for the Eastern Goldfields Province of the Archaean Yilgarn Block, Western Australia. Geol. Survey West. Aust. Record 1973/8.

Wilson H.D.B., Andrews P., Moxham R.L., Ramlal K. (1965) Archaean volcanism in the Canadian shield. Can. J. Earth Sci. 2, 161-175.

Windley B.F. (1973) Crustal development in the Precambrian. Phil. Trans. Roy. Soc. London (A) 273, 321-341.

Woodall R.W. (1965) Structure of the Kalgoorlie Goldfield. In Geology of Australian Ore Deposits, (editor J. McAndrew), pp. 71-79. 8th Comm. Min. Metall. Congr., Melbourne.

Zachariasen W.H. (1954) In The Actinide Elements. McGraw-Hill.

Additional references

Norrish K. and Hutton J.T. (1969) An accurate X-ray spectrographic method for the analysis of a wide range of geological samples, Geochim. Cosmochim. Acta 33, 431-453.

Wedepohl K.H. (1971) Geochemistry. Holt, Rinehart and Winston.

Appendix

Sample details

Sample No.	Locality	Well	depth(ft.)	Formation or Unit	Age
KH1	Mt. Hunt, S. of Kalgoorlie, W.A.	-	-	Black Flag Beds[1]	Archaean
KH21	Celebration Breakaway on Celebration road, S. of Kalgoorlie, W.A.	-	-	"	"
KH30	Near Kundana mine dump, N. of Coolgardie, W.A.	-	-	"	"
KH32	N. foot of breakaway 2½ miles, 190° from Black Flag Homestead, N. of Coolgardie, W.A.	-	-	"	"
KH36	Near old mine dump, Bulong and Parkston Turnoff, E. of Kalgoorlie, W.A.	-	-	"	"
KH37	N. of KH36, N. of road	-	-	"	"
KH38	S.E. of Mt. Charlotte Mine, Kalgoorlie, W.A.	-	-	"	"
KH41	1 mile S.W. of Mungari Granite, between Kalgoorlie and Coolgardie, W.A.	-	-	"	"
KH44	3 Mile Hill, 3 miles E. of Coolgardie, W.A.	-	-	"	"

Contd.

Sample No.	Locality	Well	depth(ft.)	Formation or Unit	Age
KH47	near old mine dump, off Norseman road, 3 miles S.E. of Coolgardie, W.A.	-	-	"	"
MI1	Mt. Isa Group, Mt. Isa, Queensland	J187	1155	Magazine Shale	Middle Proterozoic
MI2	"	K194	1502	Spear-Kennedy Siltstone	"
MI4	"	H55 E DEC	2882	Native Bee Siltstone	"
MI5	"	Fe 338 South	341	Breakaway Shale	"
AO3	Amadeus Basin	Ooraminna No. 1	713-847	Arumbera Sandstone	Cambrian
AO4	"	"	849	"	"
AO5	"	"	1357-1363	"	"
AO6	"	"	2050-2058	Pertatataka	Upper Proterozoic
AO7	"	"	2355-2359	"	"
AO9	"	"	3027-3029	"	"
AO10	"	"	3437-3445	"	"
AO12	"	"	4166-4168	Areyonga	"
AO14	"	"	4649-4654	Bitter Springs	unknown
SC1	Camp Hill, Canberra, A.C.T.	A.N.U. bore hole	176	State Circle Shale	Silurian
SC2	"	"	181	"	"

Contd.

Sample No.	Locality	Well	depth(ft.)	Formation or Unit	Age
SC3	Camp Hill, Canberra, A.C.T.	A.N.U. bore hole	186	State Circle Shale	Silurian
SC4	"	"	191	"	"
SC5	"	"	196	"	"
SC7	"	"	206	"	"
SC8	"	"	211	"	"
M216	Tamworth-Barraba district, N.S.W.[2]	-	-	Baldwin	Devonian
M277	"	-	-	"	"
M282	"	-	-	"	"
M283	"	-	-	"	"
M284	"	-	-	"	"
M285	"	-	-	"	"
B10	"	-	-	"	"
PL1	Canning Basin, W.A.	Langoora No. 1	1895-1900	Poole Sandstone	Permian
PL3	"	"	2396-2411	Grant	"
PL4	"	"	3004-3012	"	"
PL5	"	"	3390-4034	"	"
PL6	"	"	4491-4502	Laurel	Carboniferous
PL7	"	"	4552-4560	"	"

Contd.

Sample No.	Locality	Well	depth(ft.)	Formation or Unit	Age
PL8	Canning Basin, W.A.	Langoora No. 1	4845-4850	Laurel	Carboniferous
PW2	Perth Basin, W.A.	Wool Mulla No. 1	3844-3846	Woodada	Triassic
PW4	"	"	4640-4642	Kockatea Shale	"
PW5	"	"	5574	"	"
PW7	"	"	6552	"	"
PW8	"	"	7526-7528	Carynginia	Permian
PW9	"	"	8065	"	"
PW10	"	"	8071	"	"
CL1	Carnarvon Basin	Learmonth No. 2	1726-1728	Giralia	Eocene
CL2	"	"	5377-5379	Wogatti Sandstone?	Jurassic
CL3	"	"	5381	"	"
CL4	"	"	5384	"	"

1 Informal stratigraphy. Several systems have been proposed (see e.g. Williams, 1970; Glikson, 1971a).

2 For exact sample locations see Chappell (1968).